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BARIUM AND RADIUM REMOVAL FROM GROUNDWATER BY ION EXCHANGE

by

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16. ABSTRACT

The primary objective of this study was to determine the applicability of weak acid exchange resin in the hydrogen form for removal of hardness, barium and radium from groundwater. Weak acid resin in the hydrogen form eliminates the addition of sodium to drinking water. The capacity of the ion exchange resin and the regeneration requirements were determined and compared with those of strong acid resins in the sodium form. Influent water contained approximately 200 mg/L as $CaCO_3$ hardness, 250 mg/L as $CaCO_3$ total alkalinity, 20 mg/L Ba^{2+} and 20 pCi/L 226 Ra.

(Ba(+2))

For the weak acid resin, both 226 Ra and Ba^{2+} were removed to levels far below the MCL's and Ba^{2+} broke through about the same time as hardness after about 600 BV of product water had been processed. Radium continued to be removed even after the resin was saturated with hardness. The regenerant dose of 8.5 meq HCl/g dry resin yielded a column utilization of 70 percent, a regeneration efficiency of 93 to 95 percent and 1.2 BV of spent brine with TDS of 19,900 mg/L per 100 BV of product water. The weak acid resin has a much higher capacity than the strong acid resin (11.5 meq/g versus 4.8 meq/g).

The use of the weak acid resin with HCl regenerant would cost \$0.15/1000 gal and \$0.08/1000 more than the strong acid resin with NaCl regenerant for a 0.1-MGD and 1-MGD system respectively.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution, and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and is a most vital communications link between the researcher and the user community.

This study was undertaken to develop technology that can be used by small water treatment plants to remove hardness, barium, and radium^{226}. Special emphasis was placed on finding an alternative to strong-acid, sodium-form ion exchange because of the amount of sodium this process adds to the treated water. The applicability of weak acid, hydrogen-form ion exchange thus was carefully studied.

Francis T. Mayo
Director
Municipal Environmental
Research Laboratory

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ABSTRACT

A study was undertaken to develop technology that can be used by small water treatment plants to remove hardness, barium, and radium^{226}. Special emphasis was placed on finding an alternative to strong acid ion exchange (which is used in the Na^+ form) because of the large amounts of Na^+ this process adds to treated water. The primary objective of this study was to determine the applicability of weak acid exchange resin for removal of hardness, barium, and radium from the types of groundwater encountered in northern Illinois. Ion exchange is particularly suited to small communities where hardness, barium, and/or radium may be a problem. The capacity of the ion exchange resin and the regeneration requirements were to be determined and compared with those of strong acid resins for the same application.

The strong acid resin in the sodium form was tested with an influent water containing approximately 200 mg/L as $CaCO_3$ hardness, 250 mg/L as $CaCO_3$ total alkalinity, 20 mg/L Ba^{2+}, and 20 pCi/L ^{226}Ra. The regenerant dose was 6.5 lb NaCl/ft^3 (4.72 meq/g dry resin), which is typical for softening applications. Application through several exhaustion-regeneration cycles led to steady-state performance; approximately 215 bed volumes (BV) of water was applied before breakthrough, and both Ba^{2+} and ^{226}Ra were removed to concentrations much lower than their maximum contaminant limits (MCL's). Ba^{2+} broke through together with the hardness, and, at a hardness concentration of 40 mg/L (at 225 BV), the 1-mg/L MCL for Ba^{2+} had been exceeded. Radium^{226} removal of less than the MCL of 5 pico-Curies (pCi)/L continued even after the resin was completely saturated with hardness. The regeneration efficiency (equivalents of hardness removed per equivalent of NaCl applied) was about 60 percent, column utilization (percent of maximum capacity used per exhaustion cycle) was 60 percent, and 2.4 BV of 16,400 TDS brine was produced per 100 BV of product water.

The weak acid resin in the hydrogen form was tested as an alternative to the strong acid resin because the latter greatly increases the amount of Na^+ in the product water. The weak acid resin has a much higher capacity (11.5 meq/g versus 4.8 meq/g for the strong acid resin). But it must be followed by CO_2 stripping and pH adjustment, and the resin does swell significantly as it is converted from the H^+ form. Application of the same water used to test the strong acid resin was used for several cycles of exhaustion-regeneration to observe steady-state behavior. Both ^{226}Ra and Ba^{2+} were removed to levels far below the MCL's, and Ba^{2+} broke through about the same time as the hardness after about 600 BV of product water had been processed. Radium^{226} continued to be removed even after the resin was saturated with hardness. The regenerant dose of 8.5 meq HCl/g dry resin yielded a column utilization of 70 percent, a regeneration efficiency of 93 to 95 percent, and 1.2 BV of spent brine with a TDS of 19,900 mg/L per 100 BV of product water.

The cost of using the weak acid resin with HCl regenerant was somewhat higher than that for using the strong acid resin in the Na^+ form. For example, the use of a strong acid resin costs approximately $1.36/1000 gal for a 0.1-MGD plant and $0.38/1000 gal for a 1-MGD system. The use of a weak acid resin will increase these costs by $0.15/1000 gal and $0.08/1000 gal, respectively.

The conclusions concerning performance of the strong acid resin for Ba^{2+} and ^{226}Ra were consistent with the performance of a municipal plant softening system and home water softeners.

The report also contains additional information on resin capacity and selectivity, accumulation of Ba^{2+} on the strong acid resin, and resin performance under a variety of operating conditions.

This report was submitted in fulfillment of Cooperative Agreement No. CR-808912 by The University of Illinois under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period September 1, 1981 to August 31, 1983, and work was completed as of August 31, 1983.

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SECTION 1

INTRODUCTION

A. Objectives of Study

The primary objective of this study was to determine the applicability of weak acid ion exchange resins for removal of hardness, barium and radium from the types of groundwaters encountered in northern Illinois. The capacity of the resin and the regeneration requirements were to be determined and compared with those of strong acid resins for the same application.

Additional tasks included (1) evaluating the performance of the strong acid resin now in use at Crystal Lake, Illinois, for hardness and barium removal, (2) determining the barium and radium removal efficiencies of strong acid ion exchange softeners used in homes, and (3) modification of the surface of activated carbon to make it selective for the removal of barium.

B. Barium Effects and Previous Research on Its Removal

1. Barium Effects

Barium is hazardous because its major targets are the liver and the bones. Barium accumulates in the bones, displacing calcium. This displacement affects the adrenal gland and its release of hormones. Action of barium on the liver results in impairment of its detoxifying function (Tarasenko, 1977). The estimated fatal dose is 550 to 660 mg as barium (Sorg and Logsdon, 1980).

Despite the toxicity of active doses of barium, very few data are available for low-level effects of barium ingestion. An EPA-sponsored survey in northern Illinois has shown that there are possible effects from drinking water with barium concentrations greater than the maximum contaminant level (MCL) of 1 mg/L. A difference was found in male blood pressures

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between those communities with 7 mg/L of barium in their drinking water supplies and those communities with 0.1 mg/L (Sorg and Logsdon, 1980). But the researchers recommend care when interpreting the results of the study, as poor controls were maintained during the research.

2. Barium Contamination of Water Supplies

Barium is usually found in trace quantities but rarely above its MCL in drinking water supplies. Most water sources contain sufficient amounts of $SO_4^{=}$ to precipitate the insoluble $BaSO_4$ salt and to maintain barium concentrations at low levels (Logsdon and Symons, 1974). In some areas of the country, most notably northern Illinois and northeastern Iowa, the average barium concentration in drinking water supplies at a few locations is 2 to 7 mg/L with a high of 18 to 20 mg/L. In northeastern Illinois, much of the drinking water is drawn from groundwater sources in the Cambrian and Ordovician Systems, and in certain areas of this aquifer, $SO_4^{=}$ is completely absent. This depletion of dissolved $SO_4^{=}$ could be due to bacterially mediated sulfate reduction that occurs under anaerobic conditions (Gilkeson, 1981).

$$2CH_2O + SO_4^{=} \xrightarrow{\text{bacteria}} 2HCO_3^{-} + H_2S$$

The presence of dissolved H_2S, a higher alkalinity, and the presence of CH_4 which is not formed until sulfate reduction is complete, all support this hypothesis (Gilkeson, 1981).

Gilkeson (1981) suggests that the sulfate in the Cambrian and Ordovician Systems was originally derived from evaporites of an earlier age and glacial processes caused the sulfate to appear in the systems. The barium, probably derived from feldspar, was possibly in high concentrations prior to this recharge of sulfate. The mixture of high sulfate waters with the high barium waters caused barite precipitation. Subsequent elimination of the $SO_4^{=}$ in the solution leads to $BaSO_4$ dissolution and an increase in barium concentration.

A large part of McHenry and Kane Counties, the northeastern and central part of DeKalb County, the western part of Lake County, and the northwestern part of Cook and DuPage County, contain groundwater drinking sources with barium concentrations in excess of the MCL, often in excess of 10 mg/L.

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There also is a very strong relationship between barium and sulfate concentrations with the sulfate concentration increasing as the barium concentration decreases (Gilkeson, 1983).

The highest barium concentrations in northeastern Illinois occur in the anaerobic zone in the Cambrian and Ordovician Systems due to confinement by various shale and dolomite groups. For example, in central DeKalb County the concentrations of barium produced from the St. Peter Sandstone and the Ironton-Galesville Sandstone stratigraphic units are above 1 mg/L. Gilkeson (1983) gathered data showing that these two stratigraphic units, two of the more productive aquifers, are quite high in barium.

As an example of the high barium concentrations present in these aquifers, in the community of Sleepy Hollow in Kane County a test well was constructed to produce groundwater from only the St. Peter group and was found to contain 13.2 mg/L barium. The well was then deepened to produce water from only the Ironton-Galesville group and it then contained 18.2 mg/L. Several wells in the Ironton-Galesville Sandstone were found to have concentrations of 3.5 to 16 mg/L (Gilkeson, 1983).

The solubility product for barite has been determined experimentally and from thermodynamic data to be $10^{-10.04}$ at 18°C (CRC Handbook, 1981). The distinguishing characteristics of $BaSO_4$ are its low solubility (~2 mg/L in water) and its specific gravity (~4.5) (Cowan and Weintritt, 1976). The low solubility of $BaSO_4$ has caused a problem in northern Illinois when untreated waters from the different rock units of the Cambrian and Ordovician Systems have been pumped together. The discrete waters have different chemical compositions; some have high barium concentrations and others have high sulfate concentrations. The combined water composition depends on the pumping schedule as the waters respond to the changing hydraulic head. As significant amounts of water with high barium concentrations are blended with those of high sulfate concentrations, $BaSO_4$ precipitation occurs in the well bores, pumps, and discharge pipes and has caused several pump failures (Gilkeson, 1983).

Most of the communities affected by high barium concentration levels are small and very few treat to remove it. Burlington, Illinois has a

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groundwater well containing a barium concentration of 2.3 mg/L. The water treatment processes for Burlington consist of chlorination, fluoridation, and polyphosphate addition to keep iron in solution (Woller, 1978). West Dundee's well number 3 has 6.5 mg/L of barium. Only chlorine and fluoride are added (Woller, 1978). Both Elgin's Slade Avenue well number 2 and Crystal Lake's wells, containing 6.5 mg/L and 8-18 mg/L of barium, respectively, are softened, chlorinated, and fluoridated (Woller, 1976, 1978).

3. Previous Research on Barium Removal

a. Softening

Softening is an effective barium treatment process because barium is chemically similar to calcium and magnesium, the major components of hardness. Lime-soda softening, a traditional softening process, has been found to be quite effective in barium removal. The addition of lime to water raises the pH, converting the bicarbonate ions in the water to carbonate ions. The formation and precipitation of barium carbonate results in barium removal.

The percent removal of both hardness and barium by lime softening is pH dependent. Jar test studies performed by Sorg and Logsdon (1980) using Illinois groundwater with 7 to 8 mg/L of barium, indicated that removals of all three cations increased from 65 percent at pH 8.7 to a peak of 98 percent at pH 10.5. A barium removal of 87.5 percent was required to obtain a reduction to the MCL of 1 mg/L. The MCL was achieved between pH 9 and 11. The decrease in barium removal above pH 11 is due to the formation of the soluble $BaOH^+$ complex. Krause and Stover (1982) obtained similar results for barium removal by lime-soda softening. They demonstrated that with an initial barium concentration of 5.5 mg/L and a pH of 11, the barium removal was 94 percent after adding 350 mg/L of lime and 20 mg/L of alum. They hypothesized that if the raw water was aerated first to remove the free carbon dioxide, lower lime dosages could be used. The lime-soda softening process does have the disadvantages of requiring a large space for the plant and the handling of large amounts of chemicals (Downing, 1968).

Reverse osmosis is a very effective treatment process for both hardness and barium removal. The process is a membrane separation technique in which

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a semipermeable membrane allows water molecules to pass through but acts as a barrier to ions. Reverse osmosis uses pressure to force water in the opposite direction to its natural flow to produce purer water. A laboratory study conducted by Mixon on tap water containing 9.15 mg/L of barium achieved 96 to 98 percent removal using three different cellulose acetate membranes (Sorg and Logsdon, 1980). However, reverse osmosis is uneconomical for barium removal under normal conditions. Reverse osmosis could be feasible if total dissolved solids must also be reduced (Krause and Stover, 1982).

Cation exchange using natural zeolite or synthetic resin is a widespread softening method. The process includes a column containing the resin. The water to be softened usually is applied downflow to the column. After exhaustion of the column, regenerant is applied co-current or counter-current to the exhaustion cycle flow. If all flow is in the downward direction, provisions must be made to backwash the column so the resin will be loosened, deposited particles or fines produced will be flushed out, and the resin regraded. After softening, the water is generally blended with unsoftened water to obtain the desired hardness concentration.

The most commonly used resin is a strong acid resin consisting of a crosslinked polystyrene matrix with sulfonate functional groups in the sodium form (counter-ion). The selectivity series for strong acid resins indicates that barium should be removed from water before hardness. To verify that ion exchange is an effective barium removal method, the Drinking Water Research Division of the USEPA conducted a field study on two ion exchange softening plants in northern Illinois. One of the treatment plants had two ion exchange beds. The resin treated an influent water containing 10 mg/L of barium and 218 mg/L as $CaCO_3$ of hardness. Data collected from this plant showed that barium was reduced to less than 1 mg/L after 153 bed volumes (714,000 L) of water passed through the bed. Results showed that 94 to 99 percent of the barium was removed and 95 to 99 percent of the hardness was removed. The treatment cycle was terminated before either hardness or barium breakthrough occurred. After the water was blended, final barium concentrations ranged from 2.4 to 4.5 mg/L (Sorg and Logsdon, 1980).

The second treatment plant had three ion exchange beds in parallel and a raw water containing 19 mg/L barium and 230 mg/L as $CaCO_3$ of hardness.

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The exhaustion cycle of this plant was run until both barium and hardness breakthrough occurred. Barium breakthrough occurred at 100 BV and hardness breakthrough at 85 BV. At termination of the run (to 5.8 mg/L Ba^{2+} and 142 mg/L as $CaCO_3$ hardness), 70 percent of the barium and 38 percent of the hardness was still being removed. The product water was then blended with raw water to stabilize the distribution water, however, the finished water had a barium concentration range of 1.5 to 4.0 mg/L. The regeneration practices for this plant included a backwash for 10 min at 400 gpm, an application of regenerant at 28 gpm for 20 min, a slow rinse at 37 gpm for 20 min, and a fast rinse at 400 gpm for 10 min (Sorg and Logsdon, 1980).

Krause and Stover (1982) conducted bench tests to determine the usefulness of ion exchange for barium removal. They tested a strong acid resin (Amberlite 200), and a weak acid resin (Amberlite DP-1). The water to be tested contained 5.5 to 5.7 mg/L of barium. For both resin types, barium removal was at least 95 percent and all final barium concentrations were below 0.3 mg/L.

The strong acid resin is most often used in the sodium form. The resin is difficult to regenerate and if used in the hydrogen form, large amounts of concentrated acid are required for regeneration. The manufacturers of Duolite C-20, a strong acid resin, suggest that 0.5-2 gpm/ft^3 of a 4-10 percent (0.48-1.2 N) HCl or 2-8 percent (0.72-2.9 N) H_2SO_4 solution are typical for regeneration (Diamond Shamrock, 1978). These acid solutions can be corrosive and difficult to handle. These quantities of acid are equal to 5-10 lb H_2SO_4 or 4-8 lb HCl required per cubic foot of resin to be regenerated and are 2 to 3 times the stoichiometric (theoretical) amount. If the strong acid resin is used in the sodium form, the problem of handling acid is no longer present. However, 2 to 3 times the stoichiometric amount of salt regenerant is required resulting in the waste of much of the regenerant and the production of a concentrated brine solution (Diamond Shamrock, 1978). Also, if the resin is used in the sodium form, sodium is released into the drinking water.

A benefit of the weak acid resin is the ability to use it in the hydrogen form and therefore avoid adding sodium to the water. Because the weak acid resin has a higher affinity for hydrogen ions than does the strong

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acid resin, it is easier to regenerate. Therefore, less acid is required to regenerate the resin to the hydrogen form and less brine is produced. The weak acid resin only requires a small excess of regenerant (2 to 5 percent more than the capacity utilized) (see Section 5).

b. Other Processes

The process of alum and ferric sulfate coagulation should be effective for barium removal because barium sulfate has a solubility of only 2.2 mg/L (CRC Handbook, 1981). Alum and ferric sulfate coagulation are processes used for the removal of turbidity-causing substances. During coagulation the applied chemical reacts with the natural alkalinity to form aluminum hydroxide or ferric hydroxide floc. If this procedure is applied to barium-laden waters, the $SO_4^=$ released from ferric sulfate or alum should precipitate the barium cations as the solubility of $BaSO_4$ is exceeded. However, laboratory jar test studies conducted by Logsdon and Sorg (1980) showed that barium removal did not exceed 30 percent with a ferric sulfate dose of 120 mg/L and an original barium concentration of 8 mg/L. Alum produced lower removal results. Adjusting the pH had very little effect upon the results.

A second series of tests using a two-stage coagulation system was also tested. During the first stage, 100 mg/L of coagulant was added, followed by one hour of sedimentation. Then at a later time, up to 24 hours later, a second dose of 20 mg/L of coagulant was added. Even after this extensive treatment, only 80 percent of the barium was removed. If the drinking water supply exceeds a barium concentration of 5 mg/L, this process cannot be used to obtain a barium concentration below the MCL without the addition of a catalyst. Sorg and Logsdon (1980) have suggested that the low removal may be due to the slow kinetics of $BaSO_4$ precipitation.

Krause and Stover (1982) found similar results for chemical precipitation of $BaSO_4$ using alum or ferric sulfate. However, they found that the addition of $CaSO_4$ (gypsum) followed by direct filtration could give fairly good results. Using an initial barium concentration of 6 mg/L, a pH of 11.0 adjusted by NaOH addition, and $CaSO_4$ concentrations of 75 to 100 mg/L, the researchers were able to obtain a final barium concentration consistently below 1 mg/L. The addition of 0.25 mg/L of an anionic polymer as a filter

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aid enhanced barium removal. However, the high sulfate and calcium concentrations in the product water, the addition of $CaSO_4$ and NaOH, and the necessity of filters, makes this process expensive and undesirable.

Powdered activated carbon (PAC) and granular activated carbon (GAC) are traditionally used for organic removal. Neither calcium nor magnesium are adsorbed by the carbon so it has been predicted that barium would also not be adsorbed (Marayama et al., 1975). The results of laboratory tests conducted by Thiem and O'Connor (1977) using Amoco PX-121, Darco HDB, and Aqua Nuchar carbons, showed that the greatest removal of barium from the solution containing 5 mg/L Ba^{2+} was 7 percent using a 100 mg/L dose of the Amoco PX-121 carbon. GAC also can adsorb some barium but cannot be relied upon to provide efficient, cost-effective removal.

Lime-soda softening, reverse osmosis, and ion exchange softening gave the best removal results for barium. However, lime-soda softening is expensive to install and operate solely for barium removal. Reverse osmosis is also too expensive to be used solely for barium removal. The use of a strong acid resin has the disadvantages of adding sodium to the drinking water and producing a concentrated brine waste. Ion exchange is much more suited to small water supplies as it is a relatively inexpensive self-contained system that is easy to operate. To date there are no published data available for the effectiveness of using weak acid resin for barium removal. The use of weak acid resin would result in smaller quantities of brine and the elimination of sodium addition to the water. However, the operation of the weak acid resin is more complicated to operate than the strong acid resin because a strong acid is used as the regenerant and a degasifier is required to remove carbon dioxide.

C. Radium Effects and Previous Research on its Removal

1. Radium Effects

Four natural radium isotopes may be found in groundwater; $radium^{226}$, an alpha emitter with a half life of 1600 years, $radium^{228}$, a beta emitter with a half life of 5.75 years, $radium^{224}$ with a half life of 3.64 days, and $radium^{223}$ with a half life of 11.4 days. $Radium^{223}$ and $radium^{224}$ have such short half lives they are not considered a serious health hazard. Radium,

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like calcium and magnesium, is an alkaline earth metal. The body metabolizes calcium and radium similarly so ingestion of trace concentrations of radium^{226} and radium^{228} results in accumulation of radium in the skeleton. A high incidence of bone cancer has been found with ingestion of large quantities of radium^{226} and radium^{228} (Argonne National Laboratories, 1981).

To date, a correlation between low radium ingestion levels and adverse health effects has not been established, but based on the potential for such effects, the USEPA (1975) included radium in the National Interim Primary Drinking Water Regulations. The average annual gross alpha level is not to exceed 15 pCi/L. The combined radium^{226} and radium^{228} activity is not to exceed 5 pCi/L but analysis for radium^{228} is required only if the radium^{226} activity exceeds 3 pCi/L. According to the National Academy of Science (1977), a radium^{226} activity of 5 pCi/L serving one million people has an estimated health impact of 1.5 fatalities per year.

2. Radium Contamination of Water Supplies

Trace amounts of radium occur in several areas of the United States. The most notable occurrences are in northern Illinois, Iowa, central and western Florida, and in uranium mining areas in the moutain states. The radium contamination in northern Illinois is naturally occurring. Samples taken from the Cambrian and Ordovician Systems gave radium^{226} activity ranges of 0.1 pCi/L to 36.9 pCi/L and radium^{228} activity of 0.5 pCi/L to 32.7 pCi/L (Gilkeson, 1983). The highest radium concentrations were in samples drawn from the most productive stratigraphic unit, the Ironton-Galesville Sandstone.

In Florida radium has been associated with phosphate deposits. In a study of 40 drinking water supplies, Sorg (1980) showed radium^{226} activity as high as 22 pCi/L. Twenty-five of the forty supplies had activities above 5 pCi/L.

3. Previous Research on Radium Removal

a. Softening

Because radium is an alkaline earth metal and is chemically similar to barium and calcium, softening processes should be effective in radium removal

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from water supplies. Brinck (1978) studied five full-scale lime-soda softening plants in Iowa and Illinois. Measurements obtained from these plants showed radium removal efficiencies that varied from 75 to 96 percent for waters with influent radium concentrations of 5.6 to 9.3 pCi/L. The highest removals were obtained at a pH of 11. Two pilot studies by Sorg and Logsdon (1980) resulted in a 94 percent radium removal of an influent of 4.8 pCi/L at a pH of 10.5. Removal was 84 percent when the influent concentration was 4.34 pCi/L and the pH was 9.5.

Cation exchange has been shown to also be a good method for removing radium. Brinck (1978) sampled seven different ion exchange plants throughout Iowa and Illinois. Analysis showed average removals to be between 81 and 97 percent for raw waters containing 3.25 to 45 pCi/L. Strong acid ion exchange resins prefer radium over calcium (Sorg and Logsdon, 1980) so the resin should be more effective for radium removal than for hardness removal. Unlike the problem with barium treatment by ion exchange, radium^{226} was removed well enough that many plants could still blend softened and nonsoftened waters and still meet the MCL of 5 pCi/L.

Reverse osmosis has also proven effective for radium removal. Brinck (1978) found 96 percent removal of radium^{226} from a reverse osmosis plant in Iowa that had an influent of 14 pCi/L. In a study of eight reverse osmosis units in Florida, Sorg (1980) noted that radium removal efficiencies of between 87 and 98 percent were achieved when initial radium concentrations were between 3.2 and 20.5 pCi/L.

b. Other Processes

Sorg and Logsdon (1980) found that conventional alum or ferric sulfate coagulation is ineffective in radium^{226} removal in that only 0 to 25 percent was removed. However, some removal has been noted for plants removing iron and manganese. Hydrous oxides of iron and manganese have high sorption capabilities for divalent ions and radium may be removed by this process (Brinck, 1978). Tests have shown that when manganese removal is significant, radium is also reduced. In a study of seven water treatment plants employing iron and manganese removal, radium removal efficiencies ranged from 11 to 53 percent (Brinck, 1978).

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D. Description of Resins

1. Strong Acid Resin

a. Physical Description

The most commonly used strong acid ion exchange resins have crosslinked polystyrene matrices with sulfonate (SO_3^-) functional groups. The crosslinking is produced through polymerization of divinylbenzene and styrene. The sulfonate groups are produced by adding H_2SO_4 to the matrix (see Figure 1). The resins are used in either the sodium or the hydrogen form. The different forms of the resin may have different characteristics. Dowex HCR-S resin, a typical strong acid resin, produced by Dow Chemical U.S.A., will contain 44 to 48 percent water in the sodium form while the hydrogen form will contain 50 to 56 percent water. The manufacturers of Dowex HCR-S estimate that the sodium form of the resin has a capacity of 2.0 eq/L of wet resin (4.5 meq/g dry resin) and the hydrogen form of the resin has a capacity of 1.8 eq/L of wet resin (4.8 meq/g dry resin) (Dow, 1977). The strong acid resins are effective over the entire pH range since sulfonate groups are dissociated over the entire pH range.

b. Strong Acid Resin Reactions

The exhaustion reaction of the strong acid resin (Eq. 1 and 2) involves a stoichiometric exchange of cations. Regeneration of the resin is just the reverse of the exhaustion process. Because the reactions are favorable as

$$2RSO_3^- \, H^+ + Ca^{2+} \longrightarrow (RSO_3^-)_2 \, Ca^{2+} + 2H^+ \tag{1}$$

$$2RSO_3^- \, Na^+ + Mg^{2+} \longrightarrow (RSO_3^-)_2 \, Mg^{2+} + 2Na^+ \tag{2}$$

written, an excess of regenerant is required to force the reverse reaction to take place. The capacity of the strong acid resins depends not only upon the number of functional groups on the resin, but also upon the amount of regenerant applied. If low regenerant doses are used, a lower capacity will result (Bowers, 1971) because some sites are not converted back to the Na^+ form. Table 1 shows that smaller amounts of NaCl remove more cations per unit of NaCl added (higher regeneration efficiency). However, smaller amounts of NaCl used during regeneration result in a lower capacity that can be used (lower column utilization). These results were calculated from

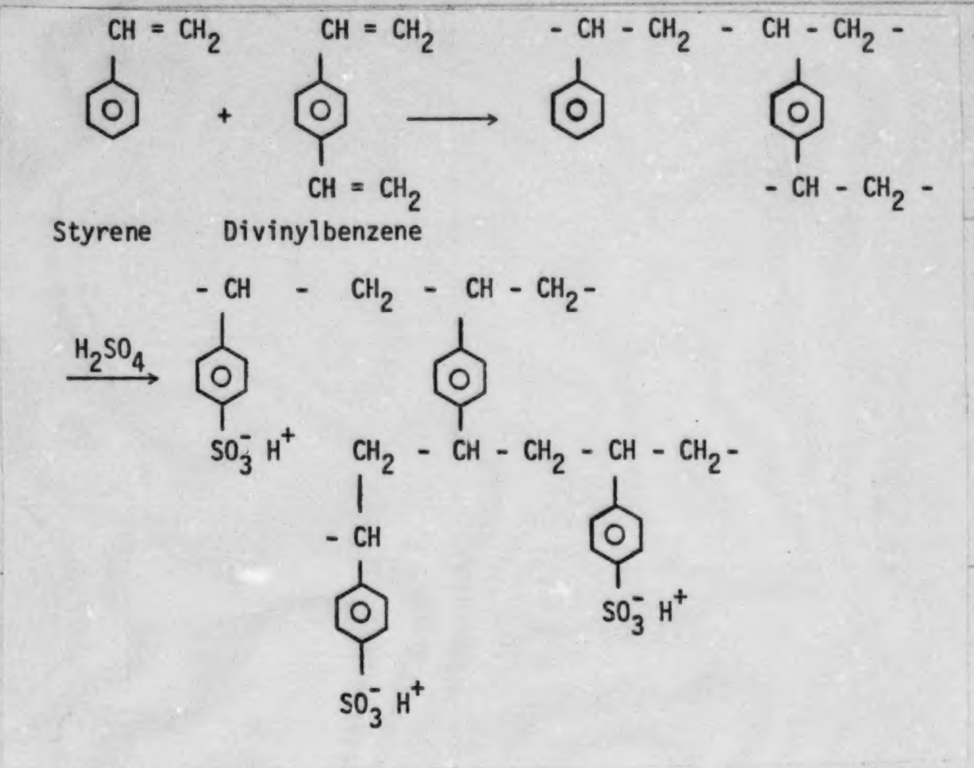

Figure 1. Preparation of strong acid ion exchange resins (Weber, 1972).

results using a typical strong acid resin with a capacity of 6.1 lb $CaCO_3/ft^3$, a raw water containing a hardness of 500 mg/L as $CaCO_3$, a loading of 2 gpm/ft^3 resin, and a 10 percent NaCl solution for regeneration (Weber, 1972).

The brines produced from strong acid resins used for softening primarily contain chlorides of calcium, magnesium, and sodium. Some iron, manganese, and aluminum may also be present (Bowers, 1971). These brine solutions, if discharged uncontrolled to waterways, can degrade stream quality by damaging aquatic life and by causing the water to be undesirable to downstream users. If brines are discharged to ponds, they can infiltrate into groundwater sources. If large slugs of brine are allowed into the sanitary sewer systems the high salt concentration can upset the biological process used in municipal wastewater treatment systems. Also high concentrations of brines can cause corrosion of mains, pumps, and equipment associated with the sewer system (Bowers, 1971).

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TABLE 1. EFFICIENCY AND COLUMN UTILIZATION AS A FUNCTION OF REGENERATION LEVEL, Na^+ FORM (WEBER, 1972)

Regeneration Level ($lb\ NaCl/ft^3$ resin)	Hardness Removed ($lb\ CaCO_3/ft^3$ resin) Theoretical	Hardness Removed ($lb\ CaCO_3/ft^3$ resin) Actual	Regeneration Efficiency (%)	Column Utilization (%)
1	0.85	0.83	98	14
2	1.70	1.32	78	22
3	2.55	1.83	72	30
5	4.25	2.85	67	47
10	8.50	3.90	46	64
15	12.75	4.65	36	76
20	17.00	5.00	29	82

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Though there are possible brine disposal methods such as evaporation ponds, uncontrolled dilution, controlled dilution, brine disposal wells, and ocean disposal, the method of brine disposal to be used in an important consideration when deciding whether to use ion exchange (Bowers, 1971).

2. Weak Acid Resin

a. Physical Description

Weak acid ion exchange resins have functional groups that are derived from weak acids such as phenolic groups, R-OH; carboxylic groups, R-COOH; and phosphonic groups, $R\text{-}PO_3H_2$ (Weber, 1972). The matrices are often polymers of divinylbenzene and methacrylic acid or acrylic acid (see Figure 2). Dowex CCR-2 manufactured by Dow Chemical is a typical weak acid resin with carboxylic functional groups on an acrylic acid-divinylbenzene matrix. The hydrogen form of the resin can contain 48 to 54 percent water. The resin has a capacity of 4.5 eq/L (9.0 meq/g dry resin) (Dow, 1977). Weak acid resins with a higher degree of crosslinking and corresponding lower capacity, do not swell as much during exhaustion cycles (Diamond Shamrock, 1978). For example, Duolite C-464 is macroporous and has a lower capacity of 3.0 eq/L. The acid ionization constant, K_a, for the weak acid resin functional groups typically fall in the range of 10^{-5} to $10^{-5.5}$. Therefore the useful pH

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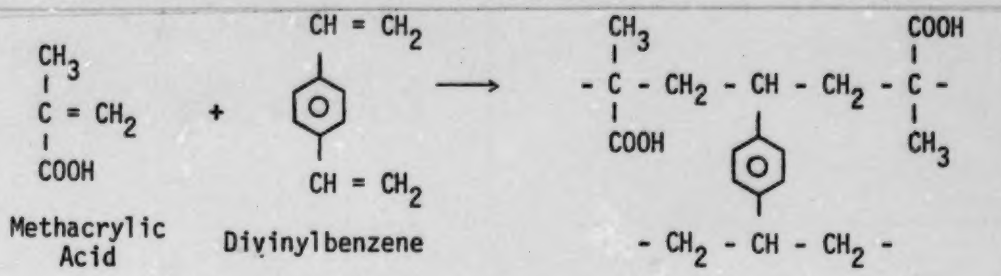

Figure 2. Preparation of weak acid ion exchange resins (Weber, 1972).

range for these resins is 5 to 14. Also weak acid resins swell considerably when changed from the hydrogen form to a metallic form, although the lower capacity resin swells less (see Table 2). The strong acid resin does not noticeably swell when changing forms. The strong acid resins also have lower capacities than the weak acid resin and their performance is not as susceptible to changes in pH.

TABLE 2. RELATIVE WATER-SWOLLEN VOLUMES FOR WEAK ACID RESINS

	Duolite C-433	Duolite C-464	Dowex CCR-2
H^+	1.0	1.0	1.0
Na^+	1.9	1.6	1.45 - 1.16
Mg^{2+}	1.5	1.4	NA
Ca^{2+}	1.2	1.2	1.15
Capacity (eq/L) (H^+ Form)	4.5	3.0	4.5

b. Weak Acid Resin Reactions

The exhaustion reactions of the weak acid resin not only include the cation exchange but also the neutralization of the released hydrogen ions. Without this neutralization, the pH decreases below the pK_a and the cation exchange ceases. If the resin is processing drinking water, the primary reaction will be the reaction in Eq. 3, where X represents Ca^{2+} or Mg^{2+}.

$$2R\text{-}COOH + X(HCO_3)_2 \longrightarrow (R\text{-}COO^-)_2\, X^{2+} + 2H_2CO_3 \qquad (3)$$

$$2R\text{-}COOH + XCO_3 \longrightarrow (R\text{-}COO^-)_2\, X^{2+} + H_2CO_3 \qquad (4)$$

$$2R\text{-}COOH + X(OH)_2 \longrightarrow (R\text{-}COO^-)_2\, X^{2+} + 2H_2O \qquad (5)$$

$$2R\text{-}COOH + XCl_2 \longrightarrow (R\text{-}COO^-)_2\, X^{2+} + 2H^+Cl^- \qquad (6)$$

The neutralization of the hydrogen ions to carbonic acid (H_2CO_3) results in the liberation of CO_2 gas. Therefore weak acid cation exchange processes must include a degasifier. Equation 6 does not go to the right because the released hydrogen ions are not neutralized and the pH of the solution drops below the pK_a; thus only cations that are balanced with alkalinity (i.e., carbonate hardess) can be removed by weak acid resins.

Some of the advantages of the weak acid ion exchange resin include the ease of regeneration and the consequential smaller quantity of brine per unit of water treated. Regeneration of the weak acid resin is the reverse of Eq. 6. Because the resin has a high affinity for the hydrogen ion, a quantity of regenerant slightly in excess of the theoretical amount (110 percent according to Peters (1983)) is required. This results in only a small amount of acid to be neutralized before discharge, and a much smaller quantity of spent brine than is produced by the strong acid ion exchange process. Downing (1968) obtained the best regeneration with 1 to 4 percent HCl solutions. If H_2SO_4 is used, lower concentrations should be used to eliminate the possibility of $CaSO_4$ or $BaSO_4$ precipitation in the resin bed. Dow Chemical U.S.A. (1977) suggests using 0.119 lb of 100 percent H_2SO_4/eq capacity utilized as a 0.5 to 1 percent H_2SO_4 solution, but they did not address the concentration of H_2SO_4 required if Ba^{2+} were present.

Although most operating ion exchange softening plants use strong acid resin there is a plant in Cheam, England that uses the weak acid resin. After a cost analysis of alternative softening options including lime-soda softening, and after excluding any processes that released sodium into the waters, the authorities of Cheam decided to use the weak acid resin. The treatment of the groundwater begins at the plant with prechlorination to 1 mg/L of chlorine (see Figure 3). After residing in 2 contact tanks, 70 percent of the flow is treated with Amberlite IRC-84 weak acid resin in

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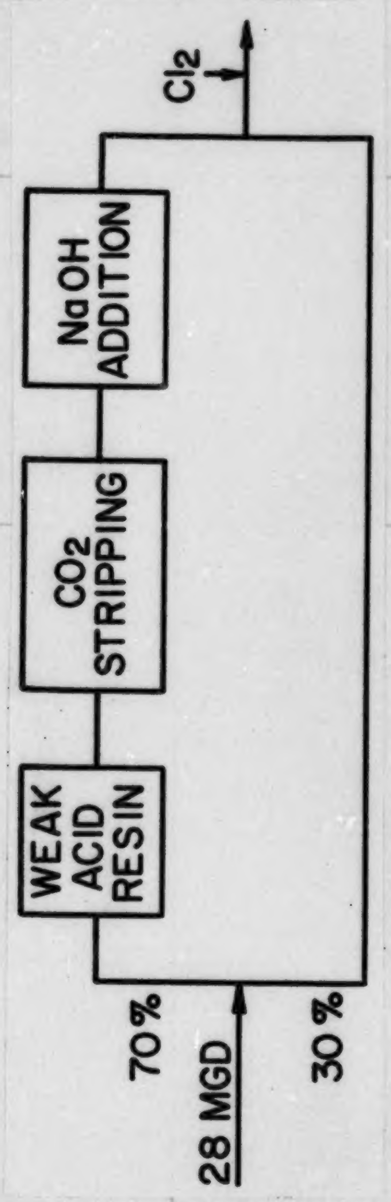
Cl_2
NaOH ADDITION
CO_2 STRIPPING
WEAK ACID RESIN
70%
28 MGD
30%

Figure 3. Flow scheme of Cheam, England treatment plant.

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6 parallel pressurized vessels, each containing 17.2 cubic meters of resin with a depth of 1.63 meters. The maximum throughput is 12.42 ML/d (3.28 MGD, 19.5 gpm/ft^2) per column. Regeneration is accomplished by first backwashing at 20.0 L/S (2.79 gpm/ft^2) for 6 min, then by applying a 4 percent HCl solution at 11.3 L/S (1.577 gpm/ft^2) for 28 min. After regeneration the columns are rinsed at 10 L/S (1.39 gpm/ft^2) for 40 min and at 100 L/S (13.95 gpm/ft^2) for 13 min. The spent regenerant is neutralized with NaOH and then pumped offsite. Two forced-air aeration towers, 7.25 meters in height are used to remove the excess CO_2 from the product of the ion exchange columns. The water is then treated with NaOH for pH adjustment and then blended with the by-passed flow to yield a final hardness of 125 mg/L as $CaCO_3$. Finally the water is chlorinated and ammoniated (Simmonds, 1980).

E. Ion Exchange Equilibrium

1. Quantification

During the cation exchange process the counter-ions (cations) are exchanged on a stoichiometric basis. There are several definitions of capacity which quantify the exchange process. One definition is the number of ionogenic groups per unit amount of ion exchange resin. However, not all ionogenic groups are available for exchange so a better definition of the maximum or total capacity is the number of ionogenic groups that are available for exchange. The units of total capacity can be either meq/g of dry resin (weight capacity) or eq/L of resin (volume capacity). It is important to specify which counter-ion is on the resin because this affects both of these capacities. Apparent capacity is the portion of the total capacity used under a specified set of experimental conditions (Helfferich, 1962). The apparent capacity is often used when considering weak acid and weak base resins because the degree of ionization, and therefore the ability to exchange the counter-ions, is pH dependent. Also an apparent capacity instead of the total capacity of the resin may be used if the resin has been incompletely regenerated.

The results of a series of batch tests in which the counter-ion x replaces counter-ion y from the resin can be graphically represented as the equivalent fraction of x on the resin versus the equivalent fraction of x in

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solution. Figure 4 contains several such curves, which are also called isotherms if the measurements are made at constant temperature. The apparent capacity of the resin for cation x under a certain set of experimental conditions is achieved when the equivalent fraction of x on the resin is 1.0.

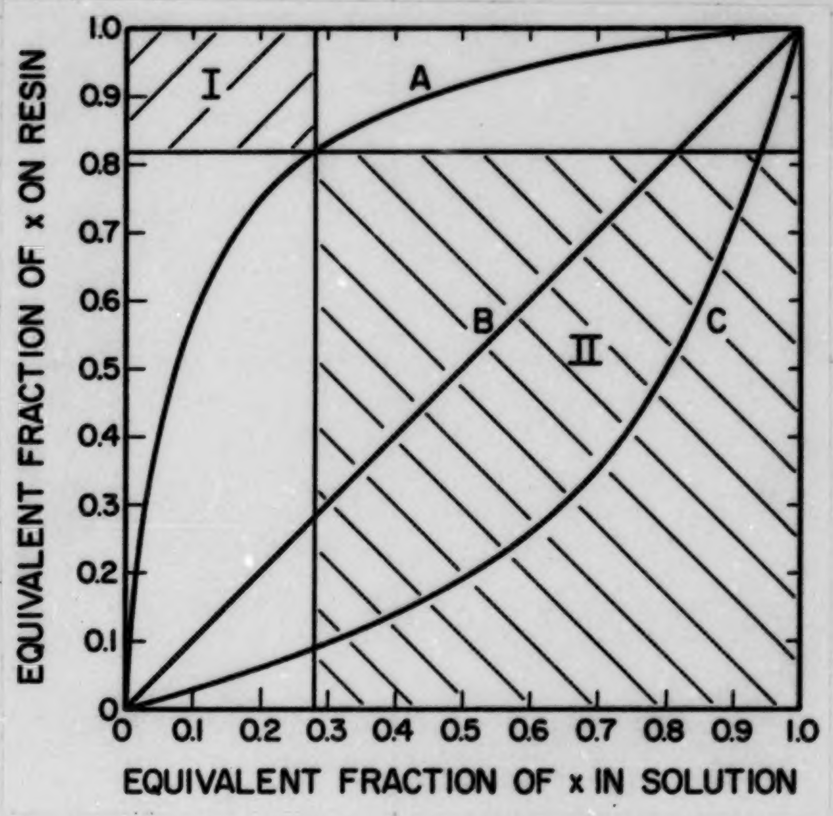

Figure 4. Ion exchange isotherms.

The selectivity of the resin indicates the preference of the resin for one ion over another. The concentration ratio of two counter-ion species in the resin is therefore different from the ratio in solution unless the resin has no preference for counter-ion x or y (curve B). If the resin prefers counter-ion x, the isotherm A will be above B. If counter-ion y is preferred, the isotherm for x, C, will be below B.

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There are several methods used to quantify the selectivity shown by the position of the isotherm. The separation factor, selectivity coefficient, and distribution coefficient are all used, but they are not true constants because they vary across the isotherm. However they can be used to assign a numerical value to the degree of selectivity. The separation factor is the quotient of the concentration ratios of the two counter-ions in the ion exchange resin and in solution;

$$\alpha_B^A = \frac{\bar{X}_A \, X_B}{\bar{X}_B \, X_A}$$

where $\bar{X}_A$ and $\bar{X}_B$ are the equivalent fractions of ions A and B on the resin, and X_A and X_B are the equivalent fractions of ions A and B in solution. The separation factor can be determined directly from the isotherm by dividing area I by area II (see Figure 4) (Helfferich, 1962).

The selectivity coefficient is a more useful constant when an exchange of ions with different valencies is occurring because it takes the change in valence into account,

$$2(R\text{-}H^+) + Mg^{2+} \longrightarrow R_2\text{-}Mg^{2+} + 2H^+$$

The selectivity coefficient contains the ionic valencies, Z_A and Z_B, as exponents.

$$K_B^A = \frac{\bar{X}_A^{|Z_B|} \, X_B^{|Z_A|}}{\bar{X}_B^{|Z_A|} \, X_A^{|Z_B|}}$$

But often the most convenient expression of equilibrium is the distribution coefficient, λ_A,

$$\lambda_A = \frac{\bar{X}_A \, \bar{m}}{X_A \, m}$$

where $\bar{m}$ is the total counter-ion concentration on the resin and m is the total counter-ion concentration in solution (Helfferich, 1962).

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2. Factors That Affect Ion Exchange Equilibrium

a. General Considerations

Selectivity depends on factors affecting the equilibrium between the species on the resin and in solution. The ions are held largely by electrostatic forces. The electrostatic force between the functional group and the counter-ion increases with the valency of the counter-ion. Therefore the more highly charged counter-ion is more strongly attracted. This preference increases with the dilution of the solution (Helfferich, 1962).

The swelling pressure of the resin and the size of the solvated ions are also important when considering ion exchange equilibrium. Resins tend to prefer smaller hydrated ions with larger ionic radii due to the elastic properties of the matrix. The preference for small hydrated ions is most pronounced when the matrix is highly strained and under high swelling pressure. More swelling occurs when counter-ions do not associate strongly with the functional groups or if the resin has a higher capacity. A high capacity resin has a higher ion concentration and consequently the solvent enters the pores in an attempt to dilute the ions. The swelling occurs even more when the solution concentration is low. A decrease in solution ion concentration increases the osmotic pressure difference between the interior of the resin and the external solution resulting in a greater solvent uptake driving force (Helfferich, 1962).

The Donnan potential is the electrostatic potential that attracts counter-ions into the resin, repels co-ions from the resin, and thus counters the tendency for ions to diffuse in response to concentration gradients. This force occurs, in the case of cation exchangers, because the cation concentration is larger in the resin and the anion concentration is greater in solution. Should these ions carry no charge, the differences in concentration would be leveled out by diffusion. However, as the ions are charged, any diffusion builds up an electric potential difference between the phases. This potential is the Donnan potential and it opposes diffusion that would completely eliminate concentration gradients. The Donnan potential partially excludes co-ions from the resin. The potential is greater when the concentration difference of the counter-ion between the resin and solution

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phases is larger. Electrolyte exclusion is also more efficient with low valence counter-ions and high valence co-ions (Helfferich, 1962).

The normal selectivity sequence, dictated by the electrostatic and swelling forces, can be disrupted by deviations from ideality. The change in a selectivity sequence can be due to various cation and anion reactions. If the functional group and the counter-ion undergo ion pair formation and association, the resin will prefer the counter-ion which forms the stronger bond with the functional group. Electrostatic localization of certain counter-ions will also cause a higher selectivity. A greater counter-ion polarizability or a functional group with a greater ability to polarize other ions can lead to a smaller radius and therefore a higher selectivity. The resin also prefers the counter-ion which associates less strongly with the co-ions in solution (Helfferich, 1962).

b. Factors That Affect the Equilibrium of Strong Acid Resins

The strong acid ion exchange resins tend to follow the theoretical considerations for cation preference. That is, the resin tends to prefer the counter-ion with the higher valency, the counter-ion with the smaller hydrated radius, the counter-ion with the greatest polarizability, the counter-ion which more strongly interacts with the fixed functional groups, and the counter-ion which is less strongly associated with the co-ion in solution. For strong acid exchangers, the selectivity series is usually $Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Mg^{2+} > UO_2^{2+}$ for divalent cations and $Tl^+ > Ag^+ > Cs^+ > Pb^+ > K^+ > NH_4^+ > Na^+ > Li^+ > H^+$ for monovalent cations (Helfferich, 1962; Sorg and Logsdon, 1980).

The high affinity of the resin for other cations than hydrogen ions causes the effects of anions to be insignificant under most circumstances. However the cation composition of the water can effect the capacity and the selectivity of the resin for the cation of interest. For instance during softening, if the sodium to hardness ratio exceeds 2 to 1, the resin capacity is lowered by sodium (Bowers, 1971).

Other species present in the water can also affect the resin performance. When organic or inorganic turbidity coats the resin particles, a loss of capacity results due to pore blockage. Turbidity can also result in excess head loss through a column causing operational problems. Iron may foul the resin by oxidizing and then precipitating as $Fe(OH)_3$ in the resin pores (Bowers, 1971).

c. Factors That Affect the Equilibrium of Weak Acid Resins

The apparent capacity of the weak acid resin has a strong dependency on the amount of alkalinity present. If during the exchange process the amount of alkalinity is depleted through neutralization of released hydrogen ions from the resin, any additional release of hydrogen ions will cause the pH to drop to a level at which additional exchange is not possible. Maximum capacity is obtained when the alkalinity in the solution is greater than the concentration of removable cations. For hardness removal, several authors found that the weak acid resin's capacity increases gradually as the hardness to alkalinity ratio increases from 0 to 0.9. From 0.9 to 0.95 the capacity increases rapidly with the best capacity at 0.95. At higher ratios the capacity is less because the final pH is lower. At lower ratios, competition between the hardness and sodium (or other cations) results in lower capacities (Downing, 1968; Vassiliou, 1968).

The capacity of the weak acid resin also depends on the type of alkalinity present. Higher capacities are obtained when the alkalinity is more basic ($OH^- > CO_3^= > HOC_3^-$) causing the pH to be higher (Downing, 1968), and a pH of 8-10 is necessary to achieve full capacity (Helfferich, 1962). Further, Na^+ can be more easily removed if pH is high.

During the uptake of a cation from a solution of a basic salt, the effect of the type of cation is of secondary importance to the neutralization and electrostatic interactions, but some specific effects are observed. Kunin (1952) has suggested that one reason for the carboxylic weak acid resins high affinity for calcium and magnesium is due to complexing of divalent cations by the carboxylic functional groups, for example.

F. Kinetics of Ion Exchange Resins

1. General Considerations

For some time, the ion exchange process was thought to be due to diffusion in accordance with Fick's law. More recently it has been realized that the ions are subject to the electric fields that they generate through diffusion.

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Therefore, the kinetics follow the Nernst-Plank equations more closely than Fick's law. One of the shortcomings of the Fick's law approach is that in order for conservation of electroneutrality to occur ($-\text{grad } C_2 = \text{grad } C_1$), where C_1 and C_2 are concentrations of ions that are being exchanged, the Fick's law coefficients (D) of each cation must be equal. But the fluxes (J) of the two cations are known not to be equal and therefore according to Fick's law the coefficients could not be equal.

$$J_2 = -D_2 \text{ grad } C_2 \neq J_1 = -D_1 \text{ grad } C_1 \text{ so } D_1 \neq D_2$$

The Nernst-Plank equations recognize that a minute deviation from electroneutrality occurs. This electrical potential gradient retards the movement of the faster cation and accelerates the slower cation resulting in electroneutrality (Helfferich, 1980).

The Nernst-Plank equations can also explain the differences between forward and reverse ion exchange rates. However, the equations are limited as they cannot explain the effects of swelling. As the resin swells and shrinks, the mobilities of the ions increase or decrease, causing the diffusion constant in the Nernst-Plank equations to vary. Swelling adds to the complexity by altering the size of the exchanger particle, thereby changing the frame of reference, the capacity per unit volume of resin (Helfferich, 1980).

The internal diffusion coefficient is an indication of the rate at which the ions move in the resin. Höll and Sontheimer (1977) found that the coefficient decreases with increasing hydrogen ion concentration, with decreasing size of the diffusion coefficient of the original counter-ion, with increasing valence, with increasing crosslinking, and with decreasing exchange capacity. Also when the solution concentration increases, the free water content of the resin decreases due to a smaller osmotic gradient across the resin surface. The decrease in the free water content results in a decrease of the co-ion diffusion coefficient but in an increase in the counter-ion diffusiob coefficient. This increase causes the counter-ion to have a greater mobility (Helfferich, 1962).

2. Strong Acid Resin Kinetics

The exchange occurring in the strong acid resin particle is a reversible electrostatic exchange process of two cations. There is no accompanying chemical reaction. Because of this lack of chemical reaction, the process of exchange occurs uniformly throughout the resin phase (Nativ, 1975). The strong acid functional groups also have a high degree of hydration. These large hydrated volumes are surrounded by a more open resin matrix than is present in most weak acid resins. The large space causes the rate of diffusion of the exchanging cation to the functional group to be fast, causing the overall rate of exchange to be faster than that for the weak acid resin (Gregor, 1948).

3. Weak Acid Resin Kinetics

The weak acid ion exchange process, unlike the strong acid process, is accompanied by fast chemical reactions as the hydrogen ion dissociates from the carboxyl group and combines with other anions. Because of the chemical reactions the kinetic models based on Fick's law or the Nernst-Plank equations fail. Helfferich (1962) concludes that the chemical reaction inside the resin causes a sharp boundary within the particle. When the resin is in the hydrogen form, it is weakly dissociated, containing few free ions. The ionic character of the resin is evident in later stages of the exchange when the functional groups of the weak acid resin have dissociated. The exchange rate in the beginning is slow because of the low concentration gradient of free hydrogen ions and the low amount of free water in the resin (Helfferich, 1962). During the conversion process from the hydrogen form to the metallic form, the water content of the resin increases because the metal cations are dissociated from the functional groups and are strongly hydrated (Höll and Geiselhart, 1978). This increase in free water causes a swelling which progresses from the outer shells of the resin particle towards the center. Therefore, the free water has a greater mobility in the outer, already swollen shells, but the water does not enter the inner shell easily because it is still contracted. As the reaction continued, free water enters farther into the resin particle (Helfferich, 1962). Höll and Sontheimer (1977) have verified the above theory with photographs. They have also proposed a pseudo-steady-state diffusion model taking the moving boundary into account to mathematically describe the ion exchange kinetics.

The rate of ion exchange in weak acid resins is slower than in strong acid resins because there is less free water in the weak acid resin (Gregor, 1948). The rates of exchange of cation pairs on the carboxylic exchanger will

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vary with the pair. The complete conversion of the hydrogen form to the metallic form may take several weeks, but the conversion of one metallic form to another metallic form may take much less time. This phenomena is due to the fact that the hydrogen form is a weak electrolyte and does not dissociate well, but the metallic form is a strong electrolyte (Kunin, 1952). Because of the slow kinetics of the hydrogen form of the weak acid resins, one would expect column breakthrough to occur at a lower percent column utilization than for strong acid resin.

G. Ion Exchange Columns

Most ion exchange operations are carried out in columns to obtain the maximum effectiveness of the resin. The upper fresh layers of resin are in contact with the highest concentration of cations. Those cations that escape adsorption in the upper layers are removed lower in the bed. As influent continues to flow through the column, the top layers become saturated and the zone of primary adsorption moves down the column. As this zone travels downward it tends to spread out due to dispersion. Eventually some cations appear in the effluent. The plot of C/Co versus time, the breakthrough curve, is generally S-shaped. If the exchange occurring is favorable, the primary adsorption zone will be smaller and the breakthrough curve sharper because of the favorable exchange of the cations will counter-act the dispersion of the cations. An unfavorable exchange will produce a broad breakthrough curve (Weber, 1972).

Most ion exchange softening processes consist of simple vessels containing a bed of resin, operated downflow to a predetermined breakthrough point. Ion exchange columns are operated in cycles: exhaustion, backwash, regeneration, and rinse. The regeneration flow is generally co-current to the exhaustion flow. Counter-current regeneration will increase regeneration efficiency and improve effluent quality in many instances, but an ion exchange system which can be regenerated counter current is more complex (NALCO, 1979) and likely to be more expensive.

Most ion exchange columns have a higher capacity than is used. In order to maintain high regeneration efficiency and low regenerant costs, less regenerant is used than the amount required to completely regenerate the column

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(see Table 1). Therefore, after regeneration contaminants are present on the column, and during the first stages of exhaustion, some will leak from the column (NALCO, 1979). When using home softeners the cost of the salt regenerant is minor compared to the advantage of long softening cycles. However municipalities need to obtain high efficiencies to keep their costs low (Bowers, 1971).

When regenerating an ion exchange column, it is necessary to have the regenerant in contact with the resin a sufficiently long time. For strong acid resins in the sodium form, Bowers (1971) has determined that the ideal contact time lies between 25 and 45 minutes. The ideal flow rates are 0.15-1 gpm/ft^3 for a 10 to 15 percent salt regenerant.

SECTION 2

CONCLUSIONS

A. Strong Acid Resins

The strong acid resin in the sodium form will remove barium to below its MCL of 1 mg/L if it is present in water that is being softened.

Cyclic exhaustion/regeneration runs used water with a hardness and barium concentration of approximately 200 mg/L as $CaCO_3$ and 20 mg/L, respectively. A typical value of 6.5 lb $NaCl/ft^3$ (4.72 meq/g) was used to regenerate the resin. These runs showed steady-state behavior after several cycles, and analyses showed that (1) the product water contained less than 3 mg/L hardness as $CaCO_3$ and 0.2 mg/L Ba^{2+} for approximately 215 bed volumes, (2) effluent Ba^{2+} and hardness increased sharply at about 225 bed volumes, (3) effluent Ba^{2+} concentration reached a maximum of about 1.7 mg/L when effluent hardness reached a value of 40 mg/L as $CaCO_3$, (4) the regeneration efficiency (equivalents of divalent metal ions removed/equivalent of NaCl applied) was approximately 60 percent, (5) 2.4 bed volumes of waste brine with a total dissolved solids (TDS) concentration of 16,400 mg/L was produced per 100 bed volumes of product water (although no attempt was made to minimize the quantity of brine), (6) approximately 2.8 meq/g of dry resin of the resin's 4.8 meq/g maximum capacity was used for divalent metal ion removal during the exhaustion run (i.e., column utilization was about 60 percent), and (7) because of the high selectivity of the resin for Ba^{2+}, about 1 meq/g was on the resin before regeneration and only 0.2 meq/g was removed during regeneration. When the regenerant level was increased by 50 percent to 9.75 lb $NaCl/ft^3$ (7.09 meq/g), the run length was increased to 260 bed volumes, and the steady-state Ba^{2+} concentration at a hardness breakthrough of 40 mg/L as $CaCO_3$ was reduced to 1.2 mg/L. Regeneration efficiency was reduced to 46 percent, however.

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The conclusion that barium removal to below the MCL of 1 mg/L would continue as long as the resin was not exhausted for hardness removal and sufficient regenerant was applied was consistent with the observations made at the municipal ion exchange softening plant at Crystal Lake, Illinois.

The strong acid resin in the sodium form will remove radium^{226} to below its MCL of 5 pCi/L if it is present in water that is being softened. Application of 20 pCi/L in the runs described above resulted in removal to values significantly below the MCL, even after the resin was saturated with hardness and barium. There was no indication during cyclic exhaustion/regeneration runs that the radium^{226} would accumulate on the resin to levels that would cause the MCL to be exceeded during a softening run.

Performance testing of a few home ion exchange softeners also showed removal of barium and radium^{226} to below their respective MCLs. These systems were not tested at a time when the resins were exhausted with hardness, however.

The strong acid resin can be used in the hydrogen form if it is necessary to minimize sodium in the product water. If it were used, it would be necessary to strip CO_2 from the product water and adjust its pH. Acid-resistant materials would also be required. Regeneration efficiency of HCl is about the same as NaCl, and barium removal follows the same pattern as it does when NaCl is the regenerant.

B. Weak Acid Resins

The weak acid resin in the hydrogen form gives excellent removals of hardness, barium and radium^{226}, and the process does not increase the sodium content of the product water. The maximum capacity of the weak acid resin is about 2.4 times higher than the strong acid resin (11.5 vs. 4.8 meq/g). Metal ions such as Ba^{2+} do not accumulate on it during use, and essentially complete removal of divalent ions is possible with about a 5 to 10 percent excess of HCl. Also, much less spent regenerant is produced. Several disadvantages exist, however. The resin swells extensively during exhaustion, and acid-resistant materials must be used for the system because of the HCl regenerant. Only divalent ions equivalent to the alkalinity in the raw water can be removed. CO_2 must be stripped from the product water, and its

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pH must be adjusted before distribution. Also, softening using this system is likely to cost more than a system with strong acid resin in the sodium form.

Application of a water containing approximately 200 mg/L as $CaCO_3$ hardness, 250 mg/L as $CaCO_3$ total alkalinity, 20 mg/L Ba^{2+}, and 20 pCi/L radium^{226} through several exhaustion/regeneration cycles showed (1) run lengths of 600-650 bed volumes of product water, (2) appearance of Mg^{2+} first, followed by Ca^{2+} and Ba^{2+} in accordance with the selectivity series $Ba^{2+} \simeq Ca^{2} > Mg^{2+} > Na^{+}$, (3) steady-state Ba^{2+} effluent concentrations of less than 0.2 mg/L when the effluent hardness was 45 mg/L or less and the regenerant dose applied was 8.5 meq/g or more, (4) regeneration efficiency of 93 to 95 percent and removal of 99^{+} percent of the divalent ions during regeneration when 8.5 meq/g HCl was applied, (5) column utilization of 70 percent, and (6) a volume of spent acid after neutralization of 1.2 bed volumes per 100 bed volumes of product water with a TDS of 19,900 mg/L when a regenerant dose of 8.5 meq/g was added.

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The weak acid resin reduced radium^{226} from 20 pCi/L to significantly below the MCL of 5 pCi/L, and essentially all radium^{226} taken up by the resin during exhaustion was removed during regeneration.

The cost of using weak acid resin with HCl regenerant instead of strong acid resin with NaCl regenerant will increase the cost of ion exchange softening by about $1.00/1000 gallons at a 10,000-GPD facility, $0.15/1000 gallons at a 100,000-GPD facility, and $0.08/1000 gallons at a 1-MGD facility.

C. Activated Carbon

The capacity of activated carbon for barium removal can be increased by treatment of the carbon with H_2SO_4, but the capacity increase is not enough to make it cost effective.

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SECTION 3

RECOMMENDATIONS

The results of this study showed that both strong acid and weak acid resin systems can be used to remove hardness, radium, and barium from water supplies. Weak acid resins have an excellent potential for use in softening when the addition of sodium to the water is undesirable, and their use for this purpose is recommended. Because these resins have rarely been used for municipal softening, a number of questions remain to be investigated, however, and these are given below.

Research is needed to determine the performance of weak acid resins for treating water with quality characteristics other than those investigated in the study described here. All of the water tested to date was similar to the water in certain locations in northern Illinois, and it had a total alkalinity (eq/L) greater than divalent cation concentration (eq/L). Because of the promise shown by the process, other water qualities should be investigated, including (1) water with total alkalinity (eq/L) less than the divalent cation concentration (eq/L), (2) water containing Al^{3+} which may foul the resin, and (3) water with a slight supersaturation of $BaSO_4$ (such as is encountered in certain locations in northern Illinois), which may precipitate in the resin and cause fouling.

The use of H_2SO_4 instead of HCl for weak acid resin regeneration needs to be investigated because of the significant cost savings that might result (see Section 5). Conditions that would avoid precipitation of $BaSO_4$ should be established.

The performance of the lower-capacity weak acid resins that do not swell as much as the high-capacity resins should be investigated.

The performance of a weak acid resin system now in use at an industrial site should be monitored to determine the product water quality that can be

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generated over a long period of time, whether fouling problems develop, and whether the swelling properties of the resin cause difficulty in operation.

Research is needed on strong acid resins in the sodium form to determine whether water that is slightly supersaturated with $BaSO_4$ will cause fouling of the resin with $BaSO_4$ precipitate, and if so, what is the best remedial action.

The chemical stability and corrosivity of ion exchange product water needs to be studied when both strong acid and weak acid resins are used to remove hardness and barium or radium. If barium, radium or a similar cationic contaminant is not present, a portion of the water can be softened and the remainder can be by-passed and blended with the softened portion to yield water with the desired hardness and chemical stability. The presence of a contaminant such as barium or radium significantly above their MCL's will require that all the water be softened. Adjustment of pH may not be sufficient to make the product water noncorrosive. Measures to produce a stable water (such as passing a fraction of the water to be treated through a column of strong acid resin in the calcium form to remove barium and radium but not hardness, and the remainder through a softening column) should be investigated as solutions to this problem.

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SECTION 4

MATERIALS AND METHODS

A. Resin

The strong acid resin, Duolite C-20, Lot DS #08281, and the weak acid resin, Duolite C-433, Lot DS #25878, manufactured by Diamond Shamrock, Redwood City, CA were used. Table 3 shows the characteristics of the two resins. The weak acid resin in the hydrogen form has a pK_a of approximately 5.5. Below approximately pH 3.5, no uptake of cations from solution is possible. As the pH increases from about 3.5 to 8, the resin capacity also increases to its maximum value.

TABLE 3. WEAK ACID AND STRONG ACID RESIN CHARACTERISTICS

	C-20	C-433
Matrix	Polystyrene	Polyacrylic
Crosslinking	Divinylbenzene	Divinylbenzene
Functional Group	Sulfonate	Carboxylic
Capacity	4.9 meq/g	11.5 meq/g
Mesh Size	16 x 50	16 x 50
pH Range	0 - 14	5 - 14

According to data provided by the manufacturer, the resin has the relative water-swollen volumes shown in Table 4.

The resins were shipped in the sodium form and were conditioned before use by a series of saturation and regeneration cycles, performed according to manufacturer specifications. A certain amount of each resin was placed in a 5 cm diameter column and washed with 2 bed volumes (BV) of a 2 N HCl solution at a rate of 6 BV/hr to saturate the resin with hydrogen ions.

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TABLE 4. WEAK ACID RESIN, C-433, RELATIVE WATER-SWOLLEN VOLUMES

Ionic Form	Relative Volume
H^+	1.0
Ca^{2+}	1.2
Mg^{2+}	1.5
Na^+	1.9

The resin was then regenerated with 2 BV of a 1.5 N NaOH solution at a rate of 6 BV/hr. The saturation-regeneration cycle was repeated twice. The resins, once conditioned, were converted to the hydrogen form with 5 BV of 2 N HCl solution at a rate of 3.8 BV/hr. The resins were then rinsed with deionized water until the pH of the effluent water from the conditioning column reached the pH of the influent water. The resins were then stored as a slurry in Pyrex glass jars until use.

The resins used in the research were not dried before use because the heat required might affect the resin structure. When resin was needed, 50 to 75 mL of the resin slurry was removed from the glass jar and excess free water was removed from the resin by vacuum filtration. Each time the resin was used, the amount of water (up to 65 percent by weight) in a representative fraction was determined. This in turn was used to convert the mass of wet resin used in experiments to a dry mass basis. To determine the moisture content, a crucible was weighed before and after the addition of 3 to 5 g of the wet resin. The crucible and the resin were then placed in a 105°C oven overnight to dry. After removing, the crucible and the resin were again weighed. From the mass difference, the amount of free water associated with the resin could be calculated.

B. Activated Carbon

The activated carbons used in this research were the 20 x 40 U.S. Standard mesh fraction of Nuchar WV-G from Westvaco, Covington, Virginia; the 8 x 16 mesh Darco 3000 from ICI, Wilmington, Delaware; and the 12 x 40 mesh Carborundum GAC 1240, from CECA, Inc., Tulsa, Oklahoma. All of the carbons were initially sieved, washed, and dried. To treat the carbon with acid,

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about 5 g of carbon were added to 500 mL of a 0.36 - 3.6 N H_2SO_4 solution. After 24 hours of shaking, the acid solution was decanted and the carbon was rinsed until the pH exceeded 4. The carbon was then vacuum filtered for 5 min and dried in a 105°C oven for 40 min. The carbon was then used in batch tests.

C. Solutions

The salts in Table 5 were used to make up the solutions used in batch tests and the column runs. An Analytical Grade of H_2SO_4, Mallinckrodt Inc., Paris, Kentucky, and the Na_2CO_3 salt were used in the alkalinity titrations. A 500 pCi/mL stock solution of radium^{226} in 4 M HCl was obtained from Dr. Philip Hopke from the Environmental Research Laboratory, University of Illinois, Urbana, Illinois. The magnesium stock solution was made by dissolving magnesium ribbon, Mallinckrodt Inc., Paris, Kentucky, in analytical reagent grade HCl and deionized-distilled water. The calcium stock solution was made by dissolving $CaCl_2$ in deionized-distilled water after drying at 120°C overnight. The barium stock solution was prepared by using $BaCl_2 \cdot 2H_2O$ that had been stored in a dessicator.

TABLE 5. SALTS USED IN SOLUTIONS

Salt	Grade	Manufacturer
$CaCO_3$	A.C.S. Reagent	M.C.B. Manufacturing Chemists, Cincinnati
$BaCO_3$	Analytical Reagent	Mallinckrodt Inc., Paris, KY
$MgCO_3$	Analytical Reagent	Mallinckrodt Inc., Paris, KY
$CaCl_2$	For Dessicators	Mallinckrodt Inc., St. Louis, MO
$BaCl_2 \cdot 2H_2O$	A.C.S. Reagent	EK Industries, Addison, IL
$MgSO_4$	Analytical Reagent	Mallinckrodt Inc., St. Louis, MO
NaCl	A.C.S. Reagent	EK Industries, Addison, IL
$NaHCO_3$	A.C.S. Reagent	EK Industries, Addison, IL
Na_2CO_3	Reagent	EK Industries, Addison, IL

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D. Analytical Methods

1. Ion Chromatography

The AutoSystem 12S Ion Chromatograph (IC), Dionex Corporation, Sunnyvale, California, was used to quantify magnesium, calcium, and barium. The system combines the separation ability of ion exchange resins with conductrimetric detection. The system consists of a programmable automatic sampler, a conductivity meter, an eluent pump, a sample pump, a regenerant pump, a chart recorder, and reservoirs for liquid storage. The separator column was a 6 x 250 mm column with a resin volume of 6 mL and a capacity of 0.2 meq/g. The suppressor column was a 9 x 250 mm column with a volume of 14 mL and a capacity of 2.8 meq/g. Figure 5 is a schematic of the system including the reactions that occur within the columns (Dionex, 1979). Standard curves were prepared for each analysis and concentrations were determined using chromatographic peak heights.

After trying various eluent dilutions, a 50 percent solution of the standard eluent was chosen to give satisfactory magnesium and calcium peak separation without causing the barium peak to be too broad. The standard eluent was a 0.0025 M HCl and 0.0025 $C_2H_6(NH_2)_7 \cdot 2HCl$ solution. Using a 50 µL injection loop and the most common range (R3), the cation peaks had the characteristics shown in Table 6.

TABLE 6. HALF STRENGTH ELUENT CHARACTERISTICS

	Barium	Calcium	Magnesium
Retention Time	25 min	11 min	7 min
1981-82 Range (mg/L)	3 - 150	0.3 - 15	0.1 - 7
(M)	0.022 - 1.09	0.012 - 0.50	0.01 - 0.41
1983 Range (mg/L)	3 - 150	0.5 - 20	0.25 - 10
(M)	0.022 - 1.09	0.012 - 0.50	0.01 - 0.41

Towards the end of the second year of research the sensitivity of the IC for the cations decreased, also shown in Table 6. When peak separation was not required (only one cation in solution), the full strength eluent was used

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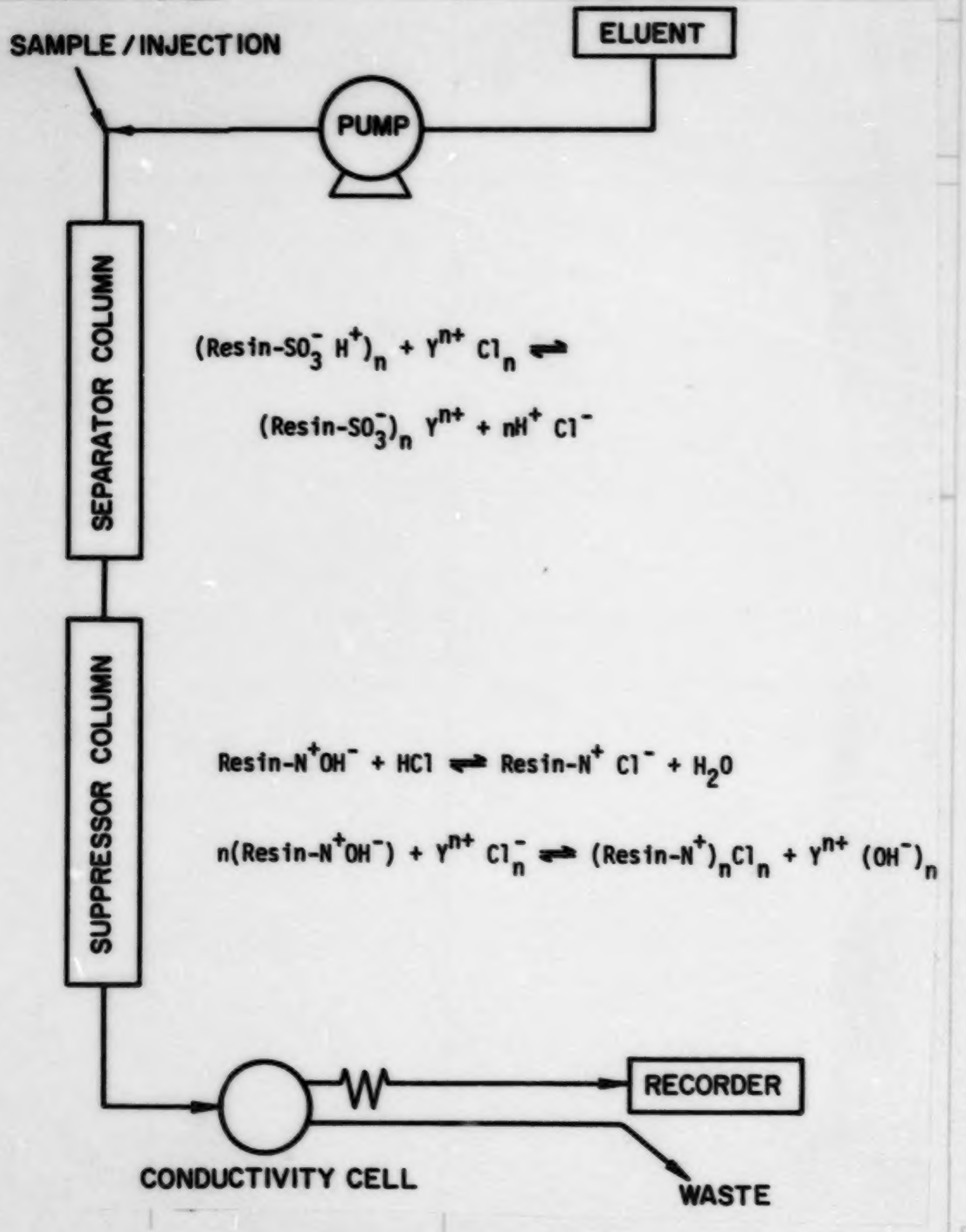
SAMPLE / INJECTION
ELUENT
PUMP
SEPARATOR COLUMN
SUPPRESSOR COLUMN
RECORDER
CONDUCTIVITY CELL
WASTE

$$(\text{Resin-SO}_3^-\ \text{H}^+)_n + \text{Y}^{n+}\ \text{Cl}_n \rightleftharpoons (\text{Resin-SO}_3^-)_n\ \text{Y}^{n+} + n\text{H}^+\ \text{Cl}^-$$

$$\text{Resin-N}^+\text{OH}^- + \text{HCl} \rightleftharpoons \text{Resin-N}^+\ \text{Cl}^- + \text{H}_2\text{O}$$

$$n(\text{Resin-N}^+\text{OH}^-) + \text{Y}^{n+}\ \text{Cl}_n^- \rightleftharpoons (\text{Resin-N}^+)_n\text{Cl}_n + \text{Y}^{n+}\ (\text{OH}^-)_n$$

Figure 5. Schematic of the ion chromatograph.

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(see Table 7). Analyses requiring the full strength eluent were made only during the first portion of the research.

TABLE 7. FULL STRENGTH ELUENT CHARACTERISTICS

Cation	Retention Time	Sensitivity Range (R3)
Barium	12 min	1 mg/L - 90 mg/L
Calcium	6 min	0.12 mg/L - 1.3 mg/L
Magnesium	4 min	0.05 mg/L - 5 mg/L

At the beginning of the research the peak heights were very reproducible. Using the full strength eluent and analyzing 3 magnesium samples, the mean concentrations and standard deviation in Table 8 were obtained. Towards the end of the research the reproducibility declined. After the suppressor column was regenerated with a 0.05 N NaOH solution, the peak heights for a given concentration would gradually increase to the values obtained just before regeneration. This increase in peak height varied from 15 to 30 percent depending upon the range used and the cation analyzed. To compensate for the change in peak height, standards were analyzed before and after a small series of samples; an appropriate value of the peak height for the standard could then be used to determine the concentration of the unknown samples.

TABLE 8. ION CHROMATOGRAPH REPRODUCIBILITY

Range	Concentration (mg/L)	Standard Deviations
10	17.55	0.062
3	2.68	0.017
3	0.86	0.0064

2. Atomic Absorption and Emission Spectroscopy

A Perkin-Elmer Model 370 Atomic Absorption Spectrophotometer (Norwalk, Connecticut) was used. Several samples were analyzed for sodium by atomic

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emission and some samples (as noted) were analyzed for barium by atomic absorption. The parameters listed in Table 9 were used in the analyses.

TABLE 9. ATOMIC ABSORPTION AND EMISSION SPECTROSCOPY PARAMETERS

	Barium	Sodium
Mode	Absorption	Emission
Wavelength	534.6 μm	589.0 μm
Oxidant-Fuel	air - acetylene	nitrous oxide - acetylene
Linear Range	< 15 mg/L	< 1 mg/L
Lamp	25 m amps	none
Additions	1000 - 2000 mg/L Na^+	none

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3. Radium Analysis

Radium samples were collected in polyethylene containers and the pH was lowered to 1.5 to 2.0 by the addition of HNO_3. The radium analyses were performed by the Environmental Research Laboratory (ERL) at the University of Illinois at Urbana, Illinois, under the supervision of Dr. Philip Hopke and by the University Hygienic Laboratory at the University of Iowa at Iowa City, Iowa, under the supervision of Dr. Rolf Hahne.

The analysis technique used by ERL was the radon emanation technique presented by Krieger and Whittaker (1980). The sample is concentrated and the $radium^{226}$ is separated by coprecipitation with barium sulfate. An EDTA reagent is then used to dissolve the precipitate and the solution is put in a sealed bubbler for ingrowth of $radon^{222}$. After ingrowth, the $radon^{222}$ is purged into a scintillation cell where the short-lived $radon^{222}$ daughters are allowed to equilibrate for 4 hours. The alpha activity is then counted using a scintillation cell which has been calibrated with a standard cell.

The University Hygienic Laboratory used an analysis technique as outlined in their Standard Operations Procedure Manual. The technique is primarily used to measure radium in clear water but it can be applied to wastewater provided the organic matter is destroyed and interfering ions are eliminated. Lead and barium carrier ($Pb(NO_5)_2$ and $BaCl_2 \cdot 2H_2O$) are added to

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a sample containing alkaline citrate. Then the radium, lead, and barium are precipitated as sulfates by the addition of sulfuric acid. The precipitate is purified by washing with nitric acid, dissolving in alkaline EDTA, and, after adjusting the pH to 4.5, reprecipitated as radium-barium sulfate. The slightly acidic EDTA keeps other naturally occurring alpha emitters and the lead carrier from precipitating. The radium which is carried by barium sulfate is determined by alpha counting with an internal proportional counter.

4. Titrations

Alkalinity was determined using the methods given in Standard Methods (1980). Some calcium and hardness samples were analyzed by EDTA titration also as specified in Standard Methods (1980).

E. Experimental Procedures

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1. Capacity Determination by Titration

Because cation exchange resins can be considered as insoluble acids, their capacity can be determined by titration with standard bases. A titration curve was developed for the strong acid resin by adding 1.0 gram resin samples to each of seven 250 mL flasks. To these flasks, successively larger amounts of a 0.1 N NaOH solution were added plus enough deionized water to make 100 mL of solution. After shaking the batch tests for 2.5 hours, the pH of the samples was measured. The titration curve was obtained by plotting the pH of the solution versus titrant added (meq/g of ion exchanger).

2. Capacity Determination by Column Studies

The barium capacity of the weak acid resin was also determined by gravity-feed column tests. Separatory funnels with glass wool in the bottom were used as the reactors. One column containing approximately 30 g of dry weak acid resin (hydrogen form) was converted to the sodium form using a 0.1 N Na_2CO_3 solution. Approximately 0.013 M $BaCl_2$ solution was passed through the column until it was saturated. The column was then rinsed with about 6 L of water. The other column contained about 10 g of the dry weak acid resin (hydrogen form) and $BaCO_3$ solution (∿0.055 M) was passed through it. The effluent from each column was collected in 2 L fractions and analyzed for barium.

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3. Batch Tests

The isotherms were determined from a series of batch tests. One hundred milliliters of the necessary solution and a range of resin and carbon weights were added to 120 mL Wheaton bottles. Within a series of batch tests, the only variable was the mass of resin or carbon. The range of weights for the strong acid resin was 0.005 to 0.30 g, for the weak acid resin, 0.005 to 0.20 g, and for the carbon, 0.01 to 0.50 g.

After the solution and adsorbent were added to the bottles, they were capped with rubber seals and crimpable aluminum caps. The bottles were then placed in a rotating shaker which inverted the bottles every few seconds to keep the system well mixed. The bottles were removed from the shaker at a predetermined time and the liquid was decanted from the resin or carbon and stored in other Wheaton bottles until analyzed. To reach complete equilibrium, it was necessary to shake the strong acid resin test bottles for a few days, but one week was used as a general procedure. The weak acid resin required a considerably longer time for equilibrium to be reached. After six weeks, no further change in barium concentration was observable (see Figure 13). It was assumed that six weeks were required for equilibration of calcium and magnesium. The equilibrium time was significantly less for barium if other salts were present, and these tests were terminated after three weeks.

4. Column Studies

The column assembly consisted of 2.5 cm inside diameter glass columns which were 75 cm in length. The columns had stopcocks on each end and the resin beds were supported by Pyrex glass wool plugs. Influent water was pumped through vinyl tubing using FMI (Fluid Metering Inc., Oyster Bay, NY) pumps. The same pumps with Teflon tubing were used to pump regenerant solutions and the deionized rinse water. Column studies were conducted using the strong acid resin in the sodium and hydrogen form and the weak acid resin in the hydrogen form.

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SECTION 5

RESULTS AND DISCUSSION

A. Strong Acid Resin Capacity and Selectivity

1. Capacity and Selectivity Determinations

The capacities of the resins used in this study were determined in order to obtain the parameters that could be related to performance. For the strong acid resin two methods were used. A pH titration curve (see Figure 6) was determined from a series of batch tests each containing 1.0 g of the hydrogen form of the wet resin in NaOH solution. The endpoint of the titration occurred at 2.75 meq Na^+/g wet resin. Taking the moisture content of the resin into account (42 percent), the capacity of the hydrogen form of the strong acid resin was determined to be 4.74 meq/g dry resin. This value corresponds to the value of 4.79 meq/g that was obtained from the single salt isotherms (see below. The average of the two capacity values was rounded to 4.8 meq/g for most calculations.

The single salt isotherms determined for the strong acid resin in the hydrogen form are shown in Figure 7. These isotherms were determined by varying the amount of resin added to solutions containing the sale of one cation. The solutions contained 5.0 meq/L of either barium chloride, calcium chloride, magnesium sulfate, or aodium bicarbonate. The horizontal axis of the isotherm is the concentration of the cation in the batch test after equilibrium divided by its initial concentration. The vertical axis is the number of equivalents of cation removed by the resin divided by the capacity of the resin in equivalents. For the sodium tests, the concentration of sodium removed was determined from alkalinity measurements to simplify the analytical procedure. This was possible because of the 1:1 correspondence between sodium and alkalinity concentration change for the reaction.

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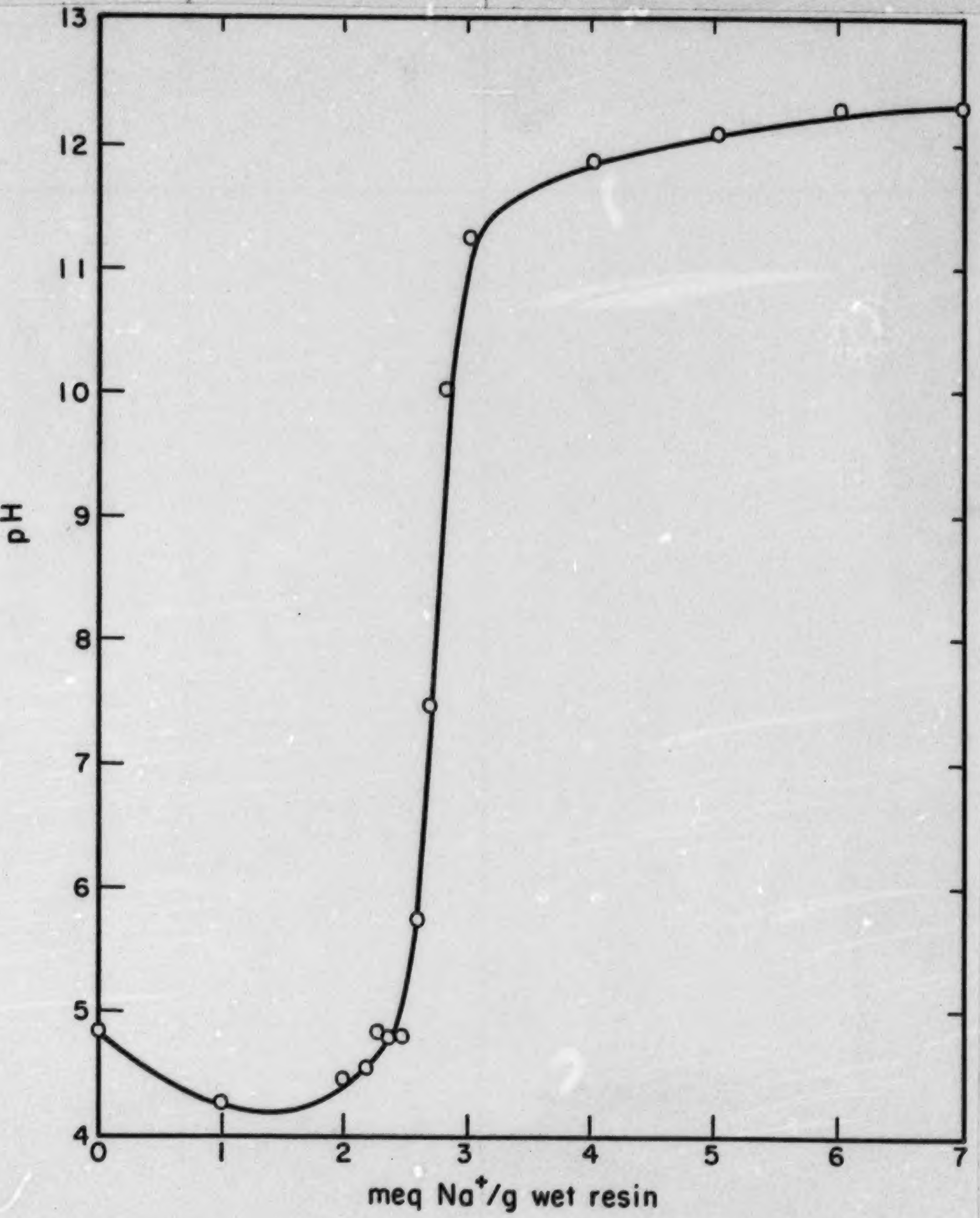

Figure 6. pH titration curve of strong acid resin.

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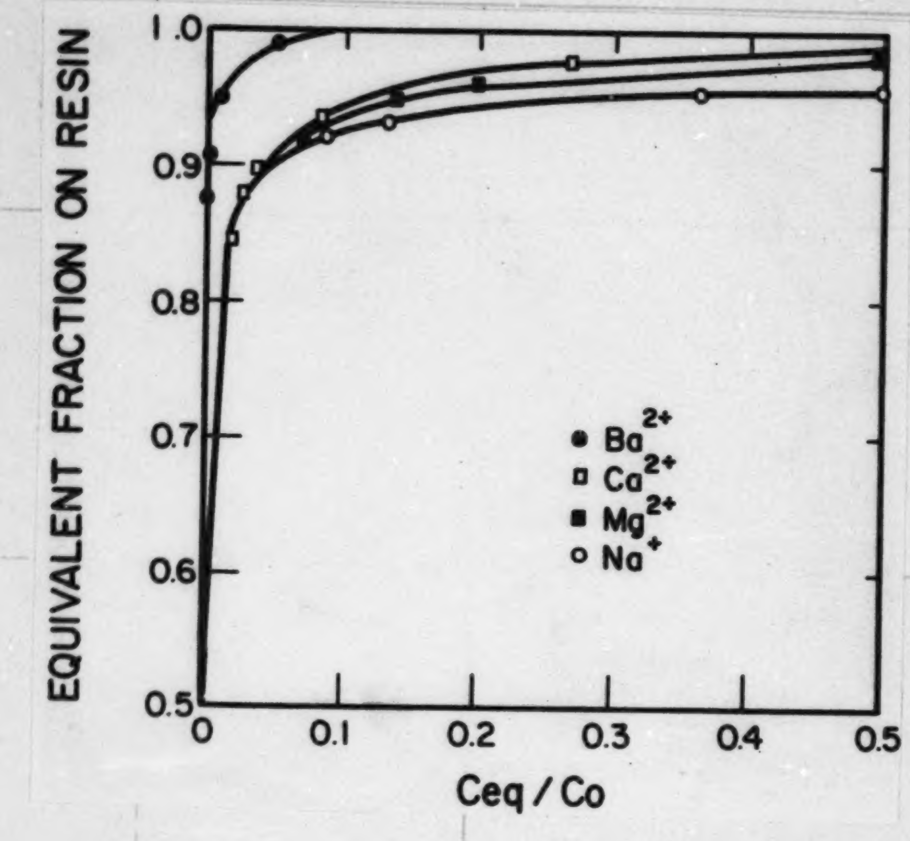

Figure 7. Strong acid single salt isotherms, H^+ form.

$$Na^+ + HCO_3^- + R\text{-}H \longrightarrow R\text{-}Na^+ + H_2CO_3$$

Figure 7 is only the upper left quadrant of the entire isotherm. If the horizontal axis is extended to a value of 1.0, all isotherms reach the capacity of 4.79 meq/g, indicated by 1.0 equivalent fraction of the cation on the resin.

The selectivity series of the resin for the various cations can also be determined from the isotherms. The greater the capacity for $C_{eq}/C_o < 0.5$, the more selective the resin is for that cation. Figure 7 shows that the strong acid resin in the hydrogen form prefers $Ba^{2+} > Ca^{2+} > Mg^{2+} > Na^+$. This selectivity series agrees with the results of others (Helfferich, 1962). The degree of selectivity can be expressed using selectivity coefficients. All selectivity coefficients for the various cations versus the hydrogen ion

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(the form of resin used) were calculated from the data at the point on the isotherm where the diagonal, (0.0, 1.0) to (1.0, 0.0), intersects the isotherm. The use of the same point on each isotherm is necessary because selectivity coefficients are not true constants and they vary across the isotherm. The values of the equivalent fraction of the cation on the resin, $\overline{X}_A$, and in solution, X_A, and the equivalent fraction of hydrogen on the resin, $\overline{X}_B$, and in solution, X_B, were used to calculate the selectivity coefficient,

$$K_B^A = \frac{\overline{X}_A^{\,|Z_B|} X_B^{\,|Z_A|}}{X_A^{\,|Z_B|} \overline{X}_B^{\,|Z_A|}}$$

where Z_A and Z_B are the charges of A and B, respectively. Further, it can be shown that

$$K_B^A / K_B^C = K_C^A$$

This method was used to develop Table 10.

TABLE 10. SELECTIVITY COEFFICIENTS (K_B^A) OF STRONG ACID RESIN CALCULATED FROM ISOTHERMS DETERMINED USING THE HYDROGEN FORM OF THE RESIN

	A				
B	H^+	Na^+	Mg^{2+}	Ca^{2+}	Ba^{2+}
H^+	-	128.7	2074	2345	50520
Na^+	0.0078	-	16.11	18.22	392.5
Mg^{2+}	0.0005	0.062	-	1.13	24.36
Ca^{2+}	0.0004	0.055	0.884	-	21.54
Ba^{2+}	2×10^{-5}	0.0025	0.041	0.046	-

A series of batch tests was also used to show how closely the selectivity coefficients calculated from isotherms in Figure 7, based on the hydrogen form of the resin, compared to selectivity coefficients calculated directly

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from isotherms of barium and magnesium that were determined using the calcium form of the resin. Table 11 shows the selectivity coefficients calculated from the isotherms from Figure 8, and the corresponding coefficients from Table 10. The two selectivity coefficients of barium versus magnesium and magnesium versus calcium are different by a factor of approximately 3. The single salt isotherms using the resin in the calcium form still show the same selectivity series as the isotherms using the resin in the hydrogen form. The coefficients obtained from Figure 8 are probably the most accurate because the shapes of the isotherms in this figure allow a more accurate determination of the amount absorbed at a given equilibrium solution concentration.

TABLE 11. SELECTIVITY COEFFICIENTS OF STRONG ACID RESIN CALCULATED FROM ISOTHERMS DETERMINED USING THE CALCIUM FORM OF THE RESIN

	Ca^{2+} Form	H^+ Form (see Table 10)
K_{Ca}^{Ba}	19.66	21.54
K_{Mg}^{Ba}	69.7	24.36
K_{Ca}^{Mg}	0.282	0.884

2. Dependence of Capacity on Ionic Strength

The composition of the water in contact with the ion exchange resin has a great effect upon its performance. The effect of ionic strength was quantified using solutions containing either Ca^{2+}, Mg^{2+}, or Ba^{2+} salts plus different concentrations of NaCl. The ionic strength at equilibrium was also affected by the number and type of ions on the resin that were exchanged for ions in solution. For the experiments described below, it was assumed that the change in ionic strength brought about by the exchange of ions was insignificant and thus that the ionic strength of the solution at equilibrium could be calculated from the concentration of salts in the solution placed in contact with the fresh resin. Ionic strength was calculated from the formula

$$I = \frac{1}{2} \sum C_i Z_i^2$$

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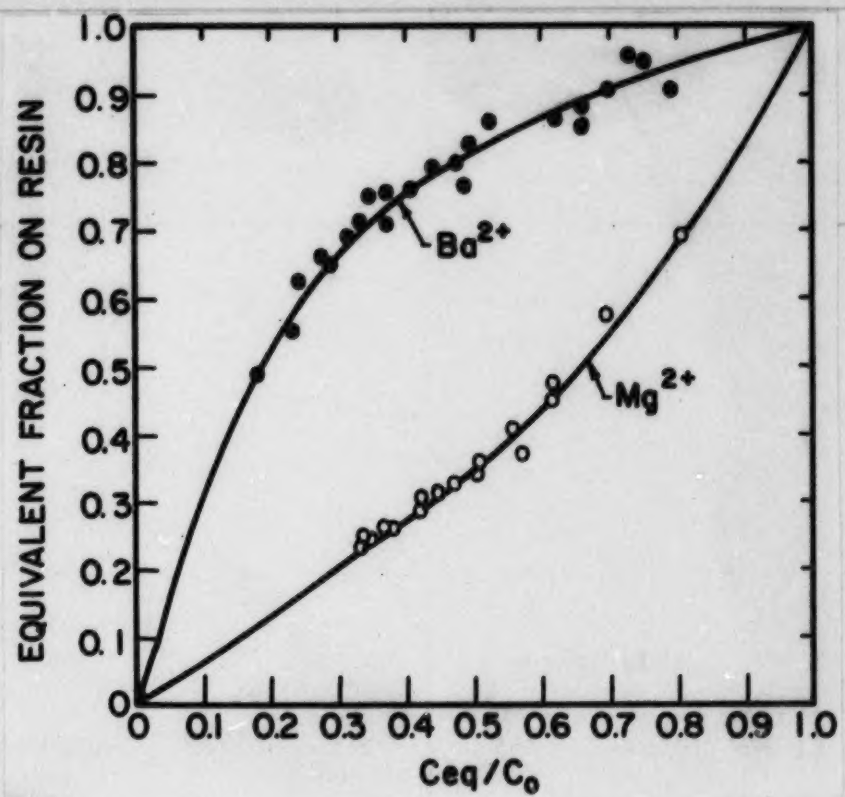

Figure 8. Strong acid single salt isotherms, Ca^{2+} form.

where C_i is the molar concentration of ion i, which has a charge of Z_i. Figure 9 shows that as I increases, the amount of sorbed Ba^{2+} decreases, presumably because Ba^{2+} and Na^+ compete for the same sites on the resin. This means that, in a full-scale ion exchange column, as the concentration of dissolved solids increases relative to Ba^{2+} concentration, the Ba^{2+} removal efficiency of the resin decreases. The extent of competition will depend on the concentration and types of cations that are present along with the Ba^{2+}. These results are consistent with the finding that if the sodium to hardness ratio exceeded 2:1, the resin capacity for hardness was lowered by the sodium (Bowers, 1971).

An increase in ionic strength has a similar effect on the magnesium isotherm (Figure 10), but the effect of a given concentration of Na^+ is much greater on the magnesium isotherm than on the barium isotherm as shown in

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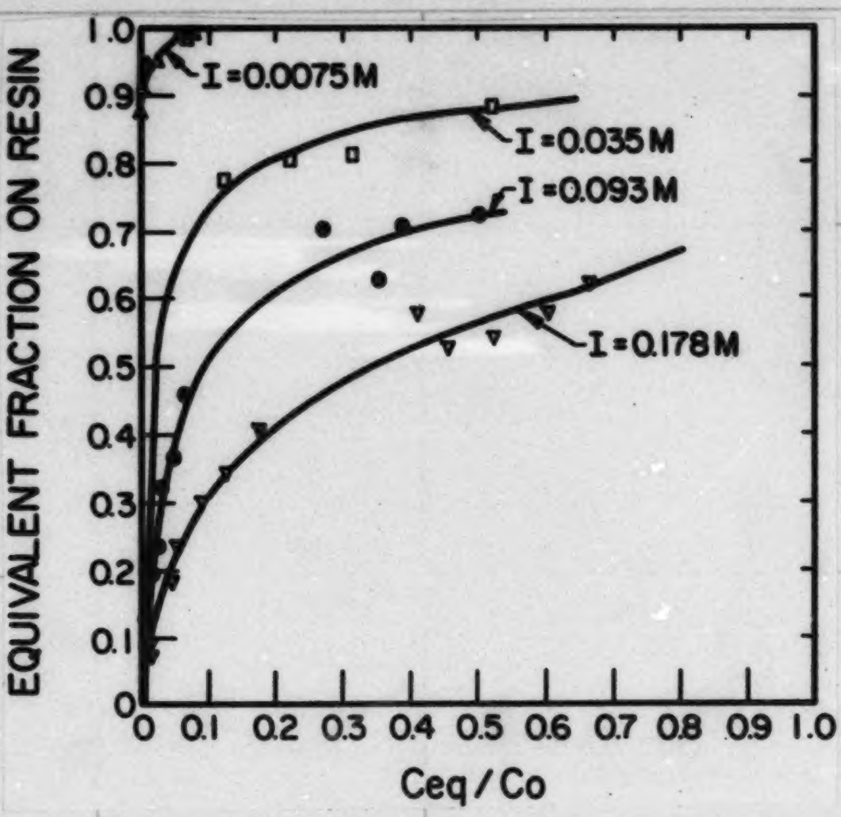

Figure 9. The effect of ionic strength on the strong acid resin isotherm for barium, H^+ form.

Figure 11. Enough sodium to raise the ionic strength to 0.178 M is required to depress the barium isotherm the same amount as a 0.06 M solution depresses the magnesium isotherm. This effect is consistent with the preference of the resin for Ba^{2+} over Mg^{2+}.

3. Dependence of Capacity on Alkalinity Concentration

Alkalinity is another constituent whose concentration varies in drinking water supplies. Batch tests were performed to observe the dependence of the capacity of the hydrogen form of the resin on the concentration of alkalinity using a solution containing approximately 1.0 mM (100 mg/L as $CaCO_3$) of Ca^{2+}, 1.0 mM Mg^{2+}, and 0.2 mM Ba^{2+} to simulate conditions in the Crystal Lake, Illinois drinking water. The alkalinity was varied to give alkalinity to divalent cation ratios (equivalent/equivalent) of 1.0 using only CO_3^{2-} salts,

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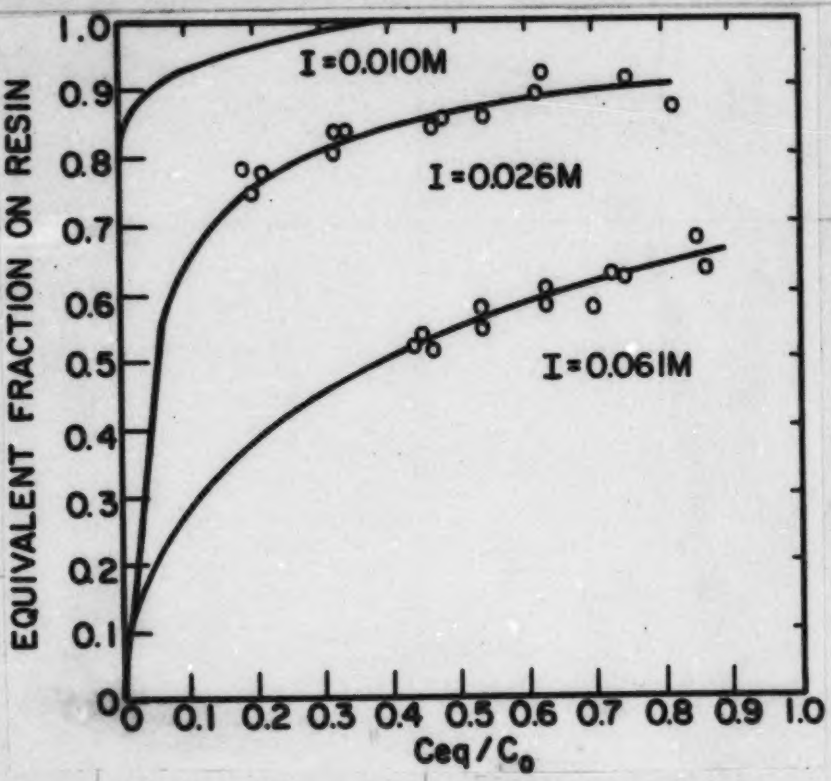

Figure 10. The effect of ionic strength on the strong acid resin isotherm for magnesium, H^+ form.

0.54 using CO_3^{2-} and Cl^- salts, and 0 using Cl^- and SO_4^{2-} salts. The results showed that the amount of alkalinity does not have a significant effect upon the resin performance.

Table 12 is the result of one batch test using a solution with an alkalinity to divalent cation ratio of 1.0 and cation concentrations of 1.098 mM calcium, 0.926 mM magnesium, and 0.175 mM barium. Regardless of the amount of resin present, a greater percentage of barium is removed than calcium or magnesium. Calcium has a greater percent removal than magnesium.

B. Weak Acid Resin Capacity and Selectivity

1. Selectivity and Capacity Determinations

The weak acid resin is not as easily characterized as the strong acid resin due to the dependence of the former on more experimental conditions.

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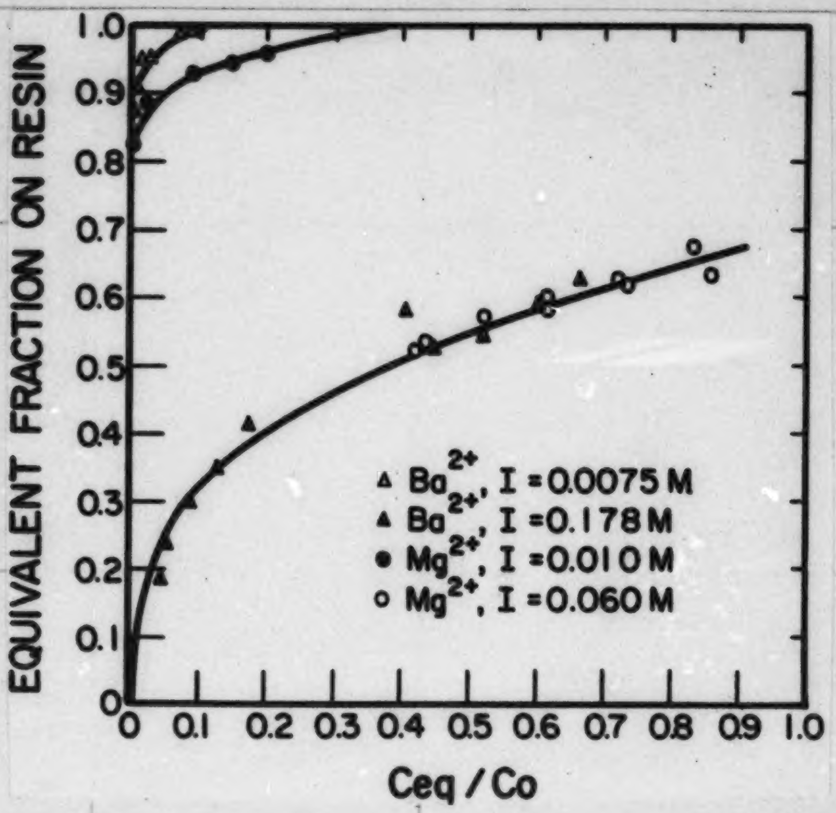

Figure 11. Comparison of the effect of ionic strength on the strong acid resin isotherms for barium and magnesium, H^+ form.

As the pH, alkalinity, and other constituents in solution change, so does the capacity of the resin. A useful method for finding the maximum capacity of the weak acid resin is to determine from isotherm data the amount of cation on the resin when an increase in solution concentration will no longer increase the amount adsorbed.

The weak acid resin requires a much longer time to reach equilibrium than does the strong acid resin. Figure 12 shows that after six weeks no change was apparent in the single salt isotherms, but various times less than six weeks show substantial differences. The batch tests used to obtain the single salt isotherms (Figure 13) were equilibrated for at least six weeks.

The single salt isotherms were developed using solutions containing 1.0 mM of either $BaCO_3$, $MgCO_3$, $NaHCO_3$, or $CaCO_3$, with the resin originally in

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TABLE 12. STRONG ACID RESIN CATION REMOVAL WITH AN ALKALINITY/DIVALENT CATION RATIO OF 1.0 EQ/EQ

Final Concentration (mM)			Percent Removal		
Mg^{2+}	Ca^{2+}	Ba^{2+}	Mg^{2+}	Ca^{2+}	Ba^{2+}
0.796	0.759	0.061	14.0	30.9	64.2
0.714	0.610	0.042	22.9	44.4	75.4
0.588	0.428	0.025	36.5	61.0	85.3
0.478	0.308	0.018	48.4	72.0	89.4
0.316	0.180	0.012	65.9	83.6	92.0
0.182	0.092	-	80.4	91.6	100
0.045	0.023	-	95.1	97.9	100

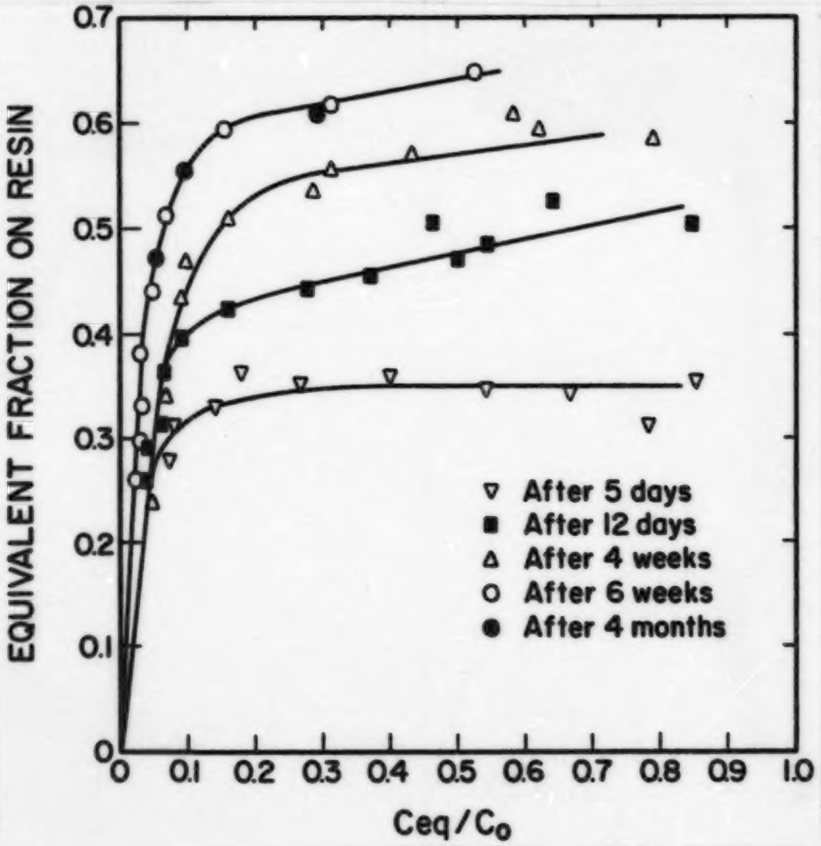

Figure 12. The effect of equilibration time on the weak acid resin isotherms for barium (single salt), H^+ form.

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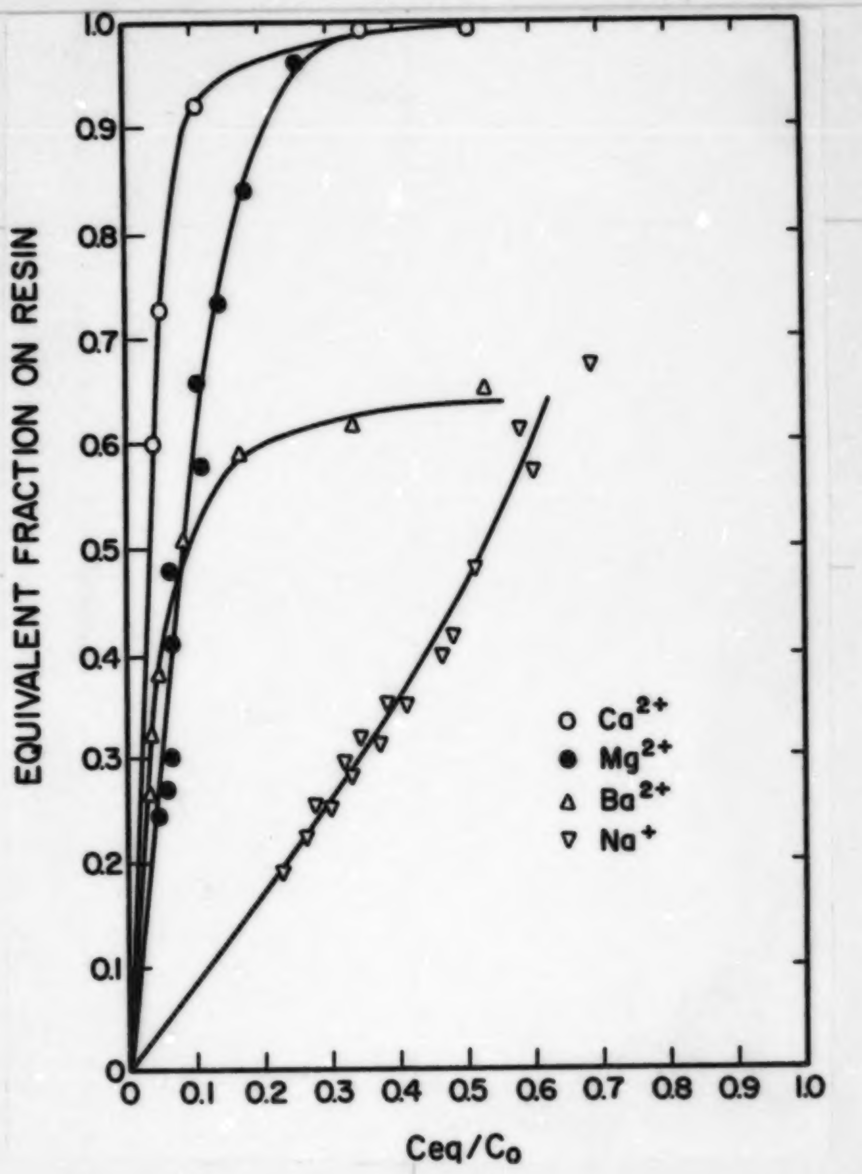

Figure 13. Weak acid single salt isotherms, H^+ form.

the hydrogen form. A maximum capacity of 11.5 meq/g was reached for calcium and magnesium, whereas a capacity of 7.5 meq/g was reached for barium. The capacity of the resin for sodium could not be calculated from the data shown in Figure 13. The calculation of equivalent fraction on the resin for these and all following isotherms use the value of 11.5 meq/g as the maximum

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capacity. A theory that explains the lower capacity for barium involves the swelling property of the resin. Under normal circumstances the larger the hydrated radius, the more the cation is excluded from the resin (Helfferich, 1962). However, if the resin swells very easily, the sorption of a large hydrated cation can cause the resin matrix to swell, opening pores and making more exchange sites available. As shown by the manufacturer's data (Diamond Shamrock, 1977), the weak acid resin swells considerably when sodium is taken up, but much less when it is saturated with calcium. The hydrated radius of an ion is inversely proportional to the ionic radius. The ionic radius of Ba^{2+} is 1.34 Å, of Mg^{2+} is 0.66 Å, and of Ca^{2+} is 0.99 Å, and thus Ba^{2+} should promote less swelling than Ca^{2+}. If the entire capacity of the resin is to be used, sufficient swelling to make all sites available to the ions must take place. Apparently the amount of swelling caused by Ba^{2+} is not sufficient to make all sites available.

Column tests were performed to compare the capacity of the weak acid resin in the hydrogen form to the capacity of the resin in the sodium form. Barium carbonate was chosen as the only salt to be in the solution that was applied to the resin because under equilibrium conditions the resin in the hydrogen form was unable to reach the same capacity for barium as for magnesium and calcium. The column test of the hydrogen form of the resin lasted for 35 days and the sodium column test lasted 7 days. The column tests showed that under these conditions, the resin in the hydrogen form had a capacity of 4.6 meq/g for barium while the resin in the sodium form had a capacity of 11.6 meq/g. The lower pH of the effluent solution (about 6.0) from the column with the hydrogen form of the resin than the pH of the batch tests (pH 7-8) probably caused the capacity from the column test to be lower than the capacity calculated from the isotherms (7.5 meq/g). The capacity determined from column tests using the sodium form of the resin is the same as the maximum capacity determined from the batch tests when Ca^{2+} and Mg^{2+} were adsorbed. The final pH of the sodium-form column test was approximately 10. The swollen condition of the sodium form of the resin thus allowed all of the exchange sites to be used by the Ba^{2+}, whereas this was not possible for the hydrogen form.

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Figure 14 shows the weak acid single salt isotherms of Figure 13 normalized using 7.5 meq/g as the maximum capacity for Ba^{2+}, and 11.5 meq/g as the maximum capacity for Ca^{2+} and Mg^{2+}. The Ba^{2+} and Ca^{2+} curves are essentially the same, indicating that the resin has essentially the same selectivity for these ions, but the Mg^{2+} curve is somewhat lower at $C_{eq}/C_o < 0.5$, indicating that it is less preferred. If the resin had been in the sodium form, the selectivity series should not differ, but Ba^{2+} should reach the same maximum capacity as Ca^{2+} and Mg^{2+}. The selectivity series for the weak acid resin, $Ba^{2+} \simeq Ca^{2+} > Mg^{2+} > Na^+$ is similar to the selectivity series for the strong acid resin, although the strong acid resin prefers Ba^{2+} considerably more than Ca^{2+}. This same selectivity series was found using a series of column runs using an influent solution containing 1.0 mM $CaCO_3$, 1.0 mM $MgCO_3$, and 0.2 mM $BaCl_2 \cdot 2H_2O$ with enough $NaHCO_3$ added to raise the alkalinity to divalent cation ratio of 1.0 eq/eq (see Section 5.D).

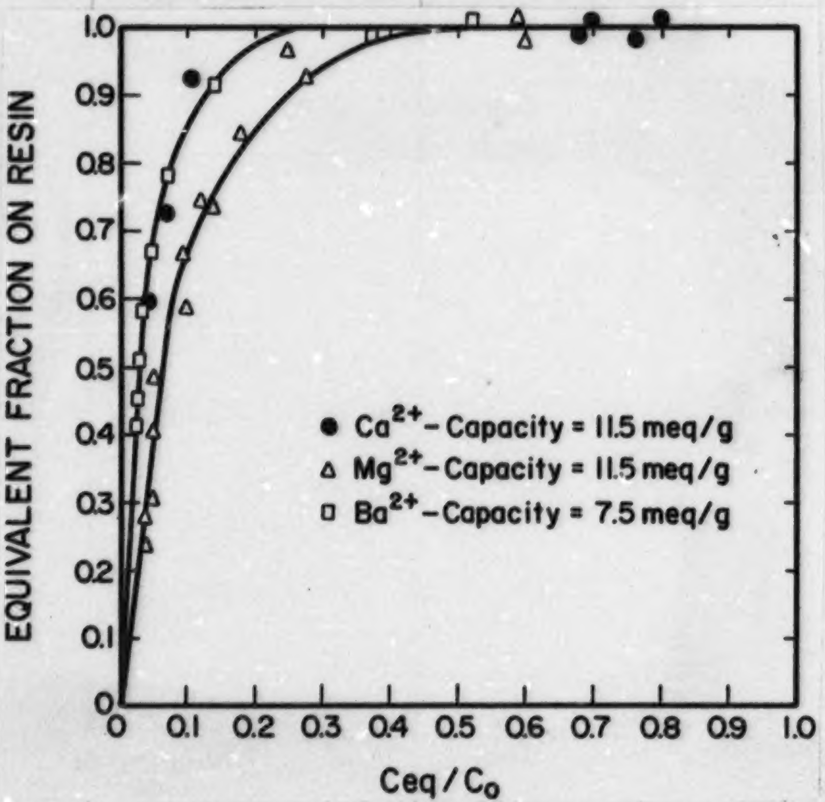

Figure 14. Weak acid single salt isotherms normalized using the maximum capacity of each cation, H^+ form.

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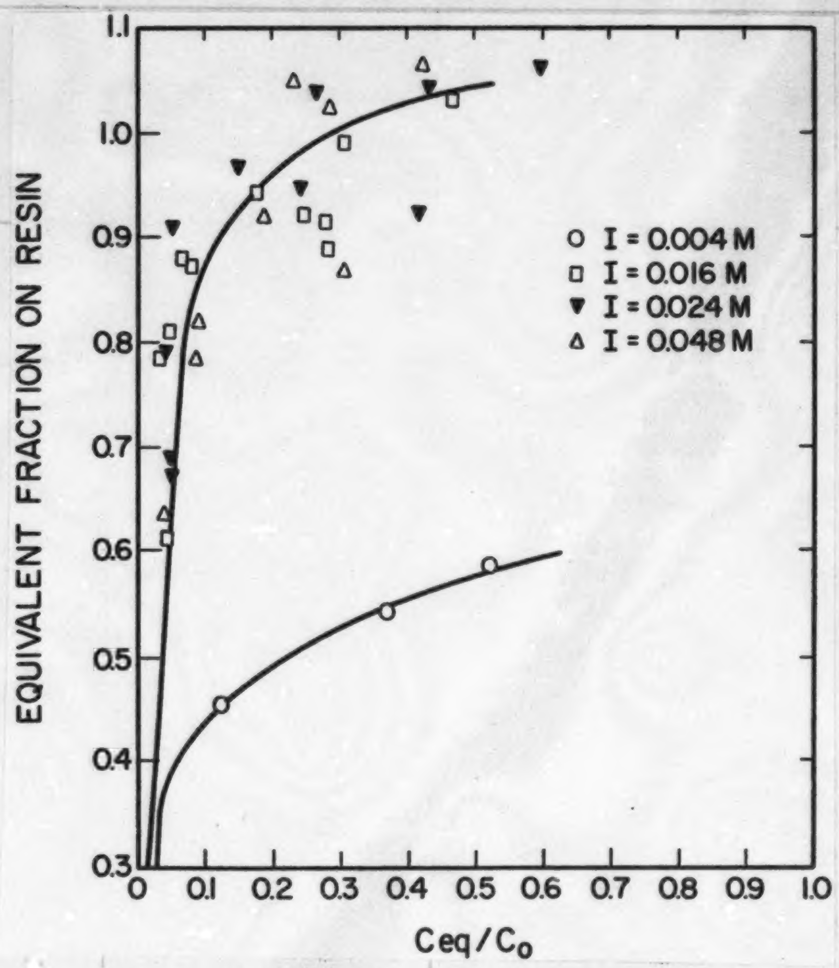

Figure 15. The effect of ionic strength on the weak acid resin isotherm for barium, H^+ form.

2. Dependence of Capacity on Ionic Strength

Sodium salts were used to vary the ionic strength of solutions so that the effect of ionic strength on capacity could be examined. Figure 15 shows the result of adding $NaHCO_3$ to a barium carbonate solution in contact with the weak acid resin. This figure shows the barium isotherm with no sodium present (I = 0.004 M) to be approaching a capacity of 7.5 meq/g. This isotherm shows less adsorption than the one from Figure 13 because it was equilibrated for only three weeks and probably had not reached true equilibrium. As sodium was added to the solution, the resin reached a capacity of approximately 11.5 meq/g for barium which is the same capacity that was achieved with single salt solutions of Ca^{2+} and Mg^{2+}. Not only was the capacity affected by the addition of sodium, but the rate of cation uptake is also affected. The addition of the sodium caused the resin to reach the maximum capacity within three weeks whereas without the addition of sodium, six weeks were required. The conversion of the sodium form of the resin to the barium form of the resin is much faster than the conversion of the hydrogen form to the barium form (Kunin, 1952).

The results of the tests to determine the effect of ionic strength can be explained by the swelling theory outlined earlier. As Na^+ is taken up by the resin, the resin swells because of its large hydrated radius. As swelling occurs, Ba^{2+} can be exchanged for H^+ and Na^+. It is assumed that because Mg^{2+} and Ca^{2+} also swell when they exchange for H^+, the addition of Na^+ to water containing Ca^{2+} or Mg^{2+} would merely result in competition between these ions and lower the capacity of the resin for Mg^{2+} and Ca^{2+}. Addition of more Na^+ than the amount required to achieve the capacity of 11.5 meq/g for Ba^{2+} should similarly result in a reduction in capacity for Ba^{2+}.

3. Dependence of Capacity on Alkalinity Concentration

The constituent in drinking water supplies which probably has the greatest effect upon the performance of the hydrogen form of the weak acid resin is alkalinity. Because of the selectivity of the resin for the hydrogen ion, there must be about as many equivalents of alkalinity present in solution as there are equivalents of cations to be removed. After all the alkalinity is removed from solution, additional cation removal is not possible because the hydrogen ion concentration in solution is too high. Several batch tests were done in order to observe what effects various alkalinity to divalent cation ratios have upon the weak acid resin's performance. The same solutions were used for these batch tests as were used for the strong acid resin alkalinity variation tests.

When the alkalinity to divalent cation ratio equaled 0, no significant removal of cations occurred. However, when the alkalinity to divalent cation ratio equaled 0.54, there were interesting results (Table 13). When small amounts of resin are used in the batch test so that alkalinity remains at the end of the test, cation removal is similar to removal when the alkalinity to divalent cation ratio equals 1.0 (Table 14). The percentage of calcium and barium that were removed were about equal, and the percentage of magnesium removed was much less, consistent with the selectivity series given above.

TABLE 13. WEAK ACID RESIN CATION REMOVAL WITH AN ALKALINITY/DIVALENT CATION RATIO OF 0.54 EQ/EQ

Influent: Ba^{2+}, 0.154 mM; Mg^{2+}, 0.992 mM;
Ca^{2+}, 1.083 mM; HCO_3^- (alkalinity), 2.407 mM

Final Concentration (mM)				Percent Removal (Percent)		
HCO_3^-	Ba^{2+}	Mg^{2+}	Ca^{2+}	Ba^{2+}	Mg^{2+}	Ca^{2+}
1.787	0.124	0.919	0.876	19.5	7.4	19.1
0.535	0.083	0.706	0.504	46.1	28.8	53.5
0.099	0.060	0.623	0.392	61.0	37.2	63.8
0.045	0.055	0.617	0.376	64.3	37.8	65.3
-0.013*	0.046	0.611	0.362	70.1	38.4	66.6
-0.105*	0.041	0.591	0.341	73.4	40.4	68.5
-0.155*	0.039	0.577	0.332	74.7	41.8	69.3
-0.269*	0.035	0.553	0.303	77.3	44.2	72.0
-0.327*	0.031	0.540	0.291	79.9	45.6	73.1
-0.341*	0.032	0.536	0.287	79.2	46.0	73.5

*A negative alkalinity is the same as mineral acidity, or H^+ concentration.

As more resin was added to the solution containing an alkalinity to divalent cation ratio of 0.54, the alkalinity was depleted and very little additional removal was noted. When the number of equivalents of divalent cations and alkalinity were equal, removal of cations continued until all cations were removed because alkalinity never became a limiting factor.

C. Strong Acid Virgin Resin Column Studies

1. First Column Study

Two column studies were conducted using virgin strong acid ion exchange resin. The first column study was run to show effluent concentration profiles

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of all cations as complete saturation on the hydrogen form of the strong acid resin occurred. This run was to yield information on the relative affinity and capacity of the resin for the various cations (Mg^{2+}, Ca^{2+}, Ba^{2+}, $^{226}Ra^{2+}$) in a column run. The results of this run were used to determine the operation of later column runs with parameters more typical of those used in practice.

TABLE 14. WEAK ACID RESIN CATION REMOVAL WITH AN ALKALINITY/DIVALENT CATION RATIO OF 1.0 EQ/EQ

Influent: Ba^{2+}, 0.150 mM; Ca^{2+}, 1.056 mM; Mg^{2+}, 0.799 mM; HCO_3^- (alkalinity), 4.01 mM

Final Concentration (mM)				Percent Removal (Percent)		
HCO_3^-	Ba^{2+}	Mg^{2+}	Ca^{2+}	Ba^{2+}	Mg^{2+}	Ca^{2+}
3.352	0.124	0.721	0.831	17.3	9.8	21.3
3.110	0.102	0.706	0.747	32.0	11.6	29.3
2.774	0.091	0.657	0.639	39.3	17.8	39.5
NA	0.070	NA	0.483	53.3	NA	54.3
NA	0.053	NA	0.319	64.7	NA	69.8
1.178	0.033	0.341	0.215	78.0	57.3	79.6
0.568	0.017	0.172	0.095	88.7	78.5	91.0
0.334	0.019	0.097	0.051	87.3	87.7	95.2
0.238	0.016	0.067	0.036	89.3	91.6	96.6
0.178	0.011	0.050	0.028	92.7	93.7	97.4

The first column had a resin bed length of 11 cm and a bed volume of 54 mL measured after saturation of the resin with the influent solution. The influent was pumped from 45 L glass carboys upflow through the column at an average rate of 5.4 mL/min (0.3 gpm/ft^2, 6 BV/hr). The average influent composition was as follows:

Na^+	197 mg/L
Mg^{2+}	92 mg/L as $CaCO_3$
Ca^{2+}	109 mg/L as $CaCO_3$
Ba^{2+}	22 mg/L
$^{226}Ra^{2+}$	20 pCi/L (estimated)

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Total Hardness	201 mg/L as $CaCO_3$
Total Alkalinity	250 mg/L as $CaCO_3$
pH	6.8 - 7.1

The influent to the column test is similar to the groundwater supply for Crystal Lake, Illinois, with the exception that their water has no ^{226}Ra and much less Na^+. The barium concentration, though quite high for most groundwater sources, is only slightly greater than the maximum values in northern Illinois groundwater (Sorg and Logsdon, 1980). An alkalinity of 250 mg/L as $CaCO_3$ (5 meq/L) was used to insure that the alkalinity would be greater than the sum of the equivalents of hardness and barium present in the influent.

The high sodium concentration in the influent was due to the use of equivalent amounts of HNO_3 and $NaHCO_3$ to adjust the initial pH of each influent batch while maintaining an alkalinity of 250 mg/L as $CaCO_3$. For subsequent column studies, CO_2 was bubbled into the influent batches to adjust the pH instead of HNO_3. This change in procedure greatly reduced the influent sodium concentration.

Samples were taken from each batch of influent and from the effluent at intervals of 80-100 bed volumes (BV) of influent applied. All samples collected were analyzed for Na^+, Mg^{2+}, Ca^{2+}, and Ba^{2+}. Sodium was measured by atomic absorption. Magnesium, calcium, and barium were measured by ion chromatography. Additional effluent samples were taken at a frequency dependent on the extent of breakthrough and were analyzed immediately for pH and alkalinity.

The breakthrough curves for the 11 cm deep resin column operated in the hydrogen form are shown in Figures 16 and 17. Breakthrough of sodium was observed first, at 180 to 185 BV of influent applied. This was followed by magnesium at approximately 450 BV, calcium at approximately 600 BV, and barium, much later, at approximately 1500 BV.

Sodium was the most weakly adsorbed ion and all sodium adsorbed was displaced by the other three cations. The magnesium ion was fairly weakly adsorbed and subsequently much of it was displaced. Only a small amount of the calcium adsorbed was displaced. No displacement of the barium was observed.

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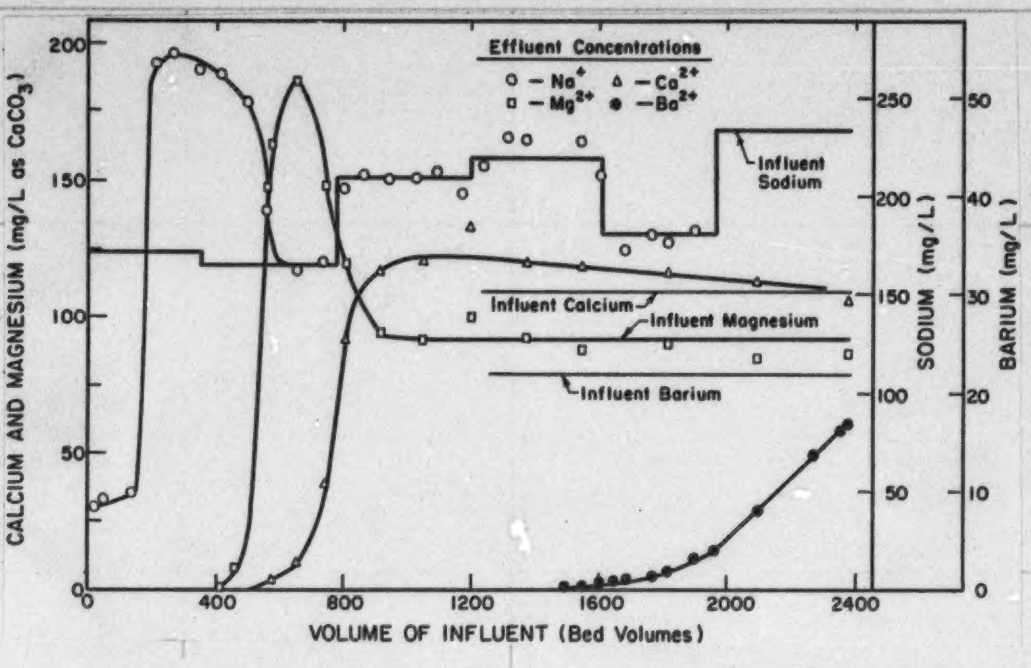

Figure 16. Breakthrough curves for Na$^+$, Mg^{2+}, Ca^{2+}, and Ba^{2+} for columns of virgin strong acid resin (1) in the hydrogen form.

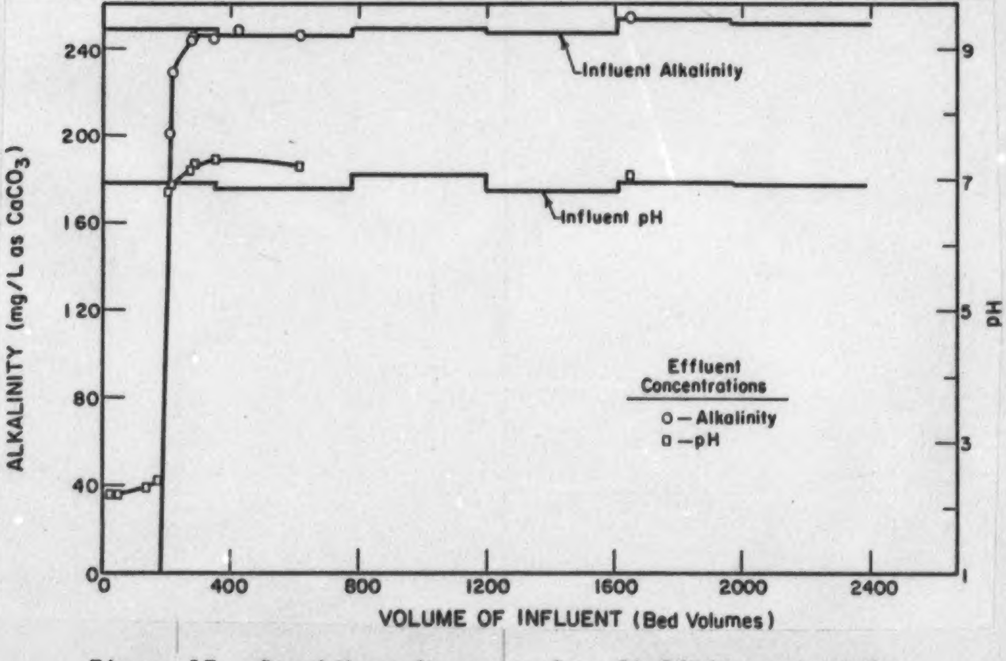

Figure 17. Breakthrough curves for alkalinity and pH for columns of virgin strong acid resin (1) in the hydrogen form.

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The observed order of breakthrough indicates a selectivity series for this strong acid resin of $Ba^{2+} > Ca^{2+} > Mg^{2+} > Na^{+}$. This agrees with results presented in Section 5.A., and with previous researchers (Helfferich, 1962).

Alkalinity breakthrough was observed at approximately 185 BV, substantially before the hardness breakthrough. This is due to the relatively high amount of sodium in the influent (197 mg/L as Na^{+}). When breakthrough of alkalinity occurs, approximately one third of the resin bed is in the divalent form (Mg^{2+}, Ca^{2+}, or Ba^{2+}) with the other two thirds converted to the sodium form. Essentially none of the resin bed remained in the hydrogen form. Due to the low pK_a of the resin, much of the exchange occurred at low pH.

Based on the areas measured under the breakthrough curves on Figure 16, the total quantities of ions removed during the column run are as follows:

Item	Quantity (meq/L of resin)
Alkalinity neutralized	1.01
Mineral acidity produced	Large amount, but not measured
Mg^{2+} adsorbed by resin	0.96
Mg^{2+} displaced during run	0.41
Mg^{2+} on resin at termination of run	0.55
Ca^{2+} adsorbed by resin	1.64
Ca^{2+} displaced during resin	0.20
Ca^{2+} on resin at termination of run	1.44
Ba^{2+} adsorbed by resin	0.69
Total divalent cations on resin at termination of run	2.68

The saturated resin column was regenerated under the following conditions:

4% nitric acid solution
78.3 bed volumes (BV) at 9.95 BV/hour, followed by
173.2 bed volumes at an average rate of 5.36 BV/hour
(251.5 BV applied total).

The regeneration was performed co-current to the direction of flow during the production run (upflow).

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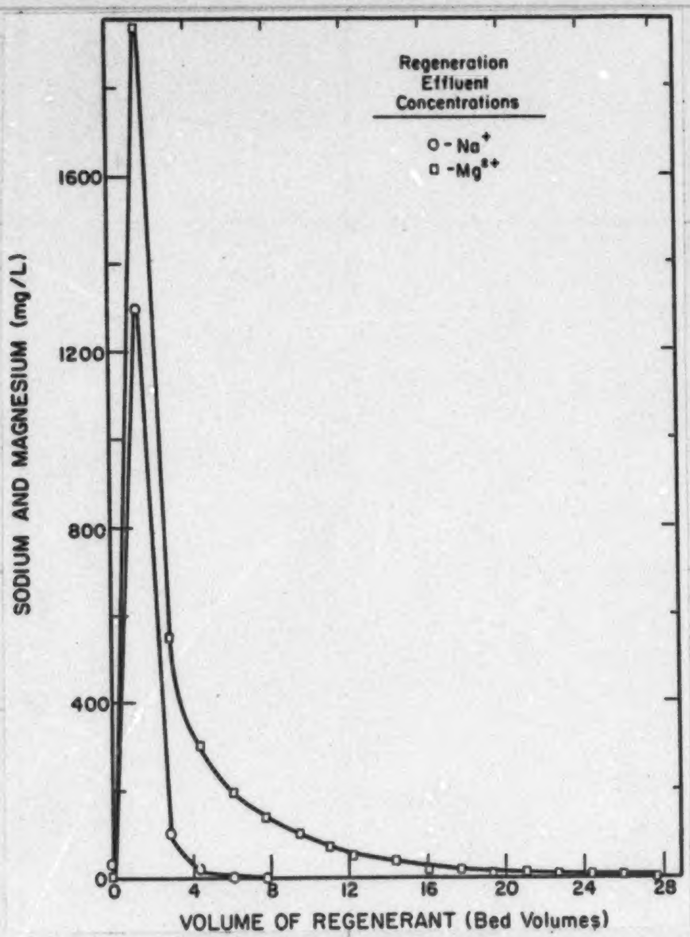

Figure 18. Removal of Na^+ and Mg^{2+} during acid regeneration of virgin strong acid resin (1).

After regenerant application of approximately seven times the equivalents of divalent cations removed by the run (4% HNO_3, 30 BV), most of the sodium, magnesium and calcium was removed from the resin. However, after application of eighteen times the amount of the resin capacity utilized (4% HNO_3, 78 BV), approximately 10 percent of the barium still remained on the resin. The application of an additional 173 BV of regenerant was required to remove the barium completely.

The co-current nitric acid solution regeneration results are shown in Figure 18 and 19. Sodium is removed with the least amount of regenerant,

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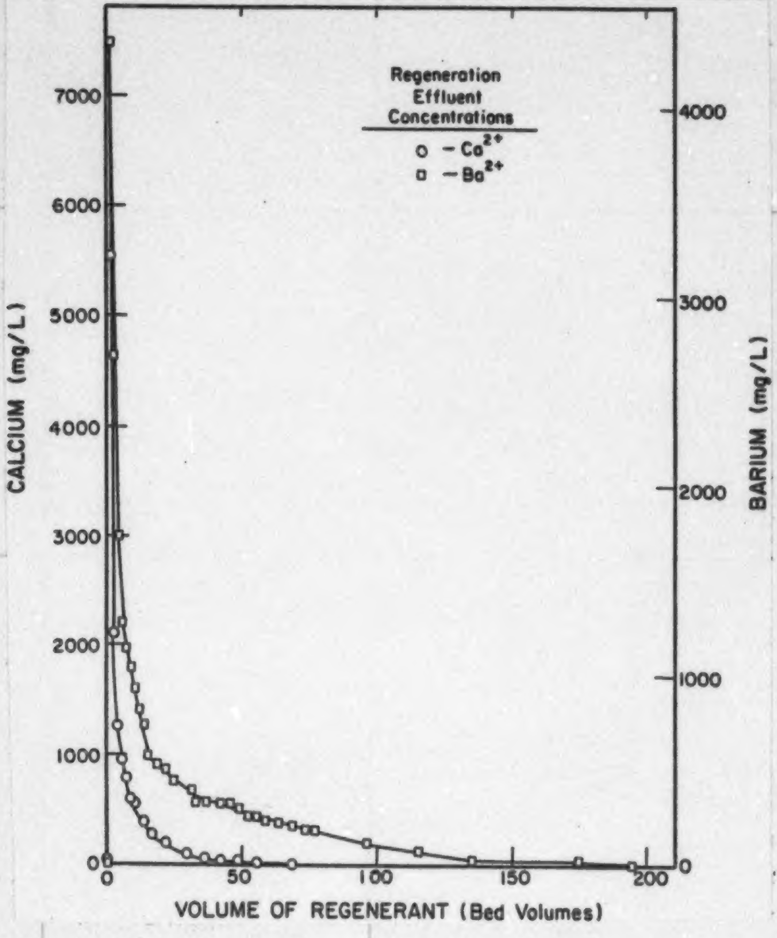

Figure 19. Removal of Ca^{2+} and Ba^{2+} during acid regeneration of virgin strong acid resin (1).

followed by magnesium and then calcium, with barium requiring the greatest amount of regenerant to completely remove it from the resin. This is in agreement with the selectivity series for this resin, $Ba^{2+} > Ca^{2+} > Mg^{2+} > Na^{+}$.

A good mass balance check on the barium applied to and removed from the resin was obtained. Barium adsorbed by the resin during exhaustion was 0.69 meq/mL of resin, while the barium found in the spent regenerant was 0.70 meq/mL of resin.

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2. Second Column Study

The second column study was conducted in deeper, 62 cm, columns until approximately 1 mg/L of Ba^{2+} appeared in the effluent. The purpose of the second column study was to determine if comparable breakthrough volumes (in BV) would be achieved for both deep and shallow columns. Bed depths of 62 cm are within the range used in practice. Both a sodium form and a hydrogen form column were tested. The sodium form resin was converted from the hydrogen form by pumping several liters of 1.5 N NaOH through the column followed by about 2 liters of de-ionized water.

The experimental parameters for the two columns are as follows:

Hydrogen Form Column

2.48 cm diameter, 61.80 cm depth
113.88 g resin (dry weight, hydrogen form)
1 bed volume - 298 mL (wet volume, hydrogen form)
Influent applied at:
21.4 mL/min (1.1 gpm/ft^2, 4.3 BV/hr) for the first 263 bed volumes, then
12.9 mL/min (0.65 gpm/ft^2, 2.6 BV/hr) for the completion of the run.

Sodium Form Column

2.48 cm diameter, 61.60 cm depth
110.77 g resin (dry weight, hydrogen form)
1 bed volume = 297 mL (wet volume, hydrogen form)
Influent applied at:
24.8 mL/min (1.2 gpm/ft^2, 5.0 BV/hr).

Influent batches were prepared in a 100 gallon stainless steel covered tank. The average influent composition for these two columns are as follows:

Na^+	40 mg/L
Mg^{2+}	90 mg/L as $CaCO_3$
Ca^{2+}	103 mg/L as $CaCO_3$
Ba^{2+}	19 mg/L
$^{226}Ra^{2+}$	15-22 pCi/L

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Total Hardness	193 mg/L as $CaCO_3$
Total Alkalinity	250 mg/L as $CaCO_3$
pH	6.9 - 7.3

Influent was pumped by a separate pump for each column, upflow through the resin beds. Samples were taken from each batch of influent and from the effluent at intervals of 60-110 BV of influent applied. The influent and effluent samples were analyzed for sodium, magnesium, calcium, and barium. Additional samples of the influent and effluent from each column were taken in 130 mL polyethylene plastic bottles for radium analysis by the Environmental Research Laboratory at the University of Illinois. For the hydrogen form resin column only, measurements were made of the effluent pH and alkalinity at a frequency dependent upon the extent of breakthrough. The application of influent to each column was stopped when the effluent barium concentration exceeded 1 mg/L.

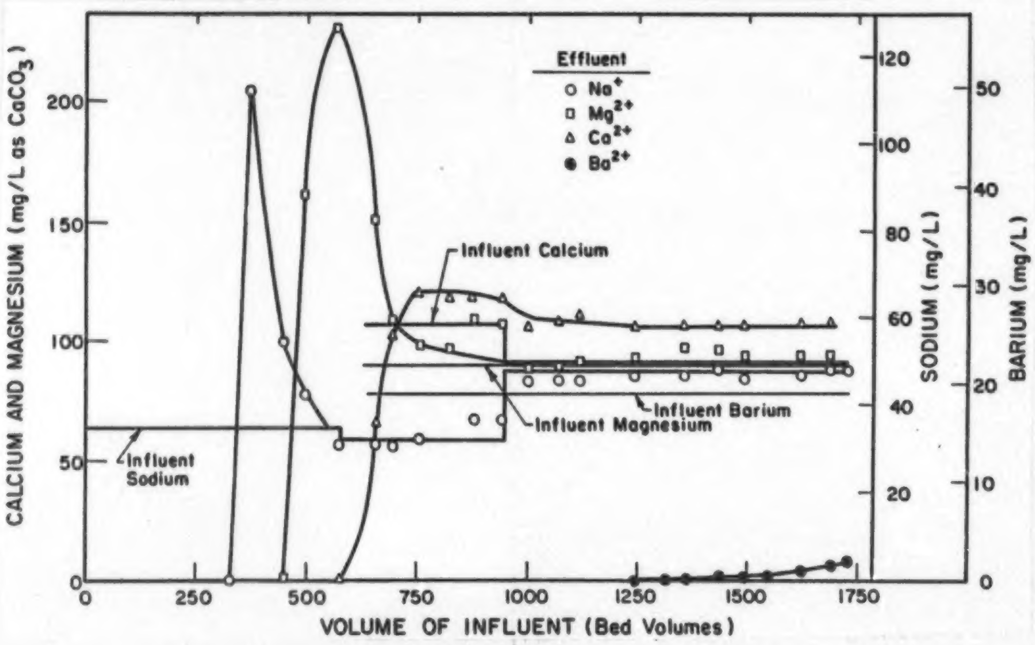

Figure 20. Breakthrough curves for Na^+, Mg^{2+}, Ca^{2+}, and Ba^{2+} for columns of virgin strong acid resin (2) in the hydrogen form.

The breakthrough curves for the hydrogen form resin column are shown in Figures 20 and 21, and for the sodium form resin column in Figure 22.

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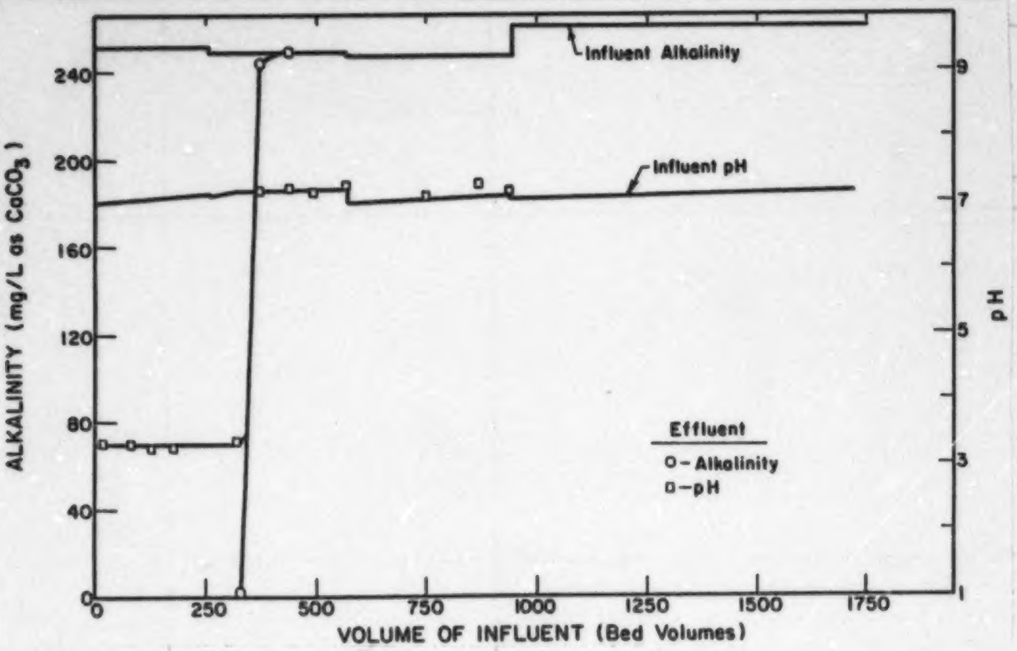

Figure 21. Breakthrough curves for alkalinity and pH for columns of virgin strong acid resin (2) in the hydrogen form.

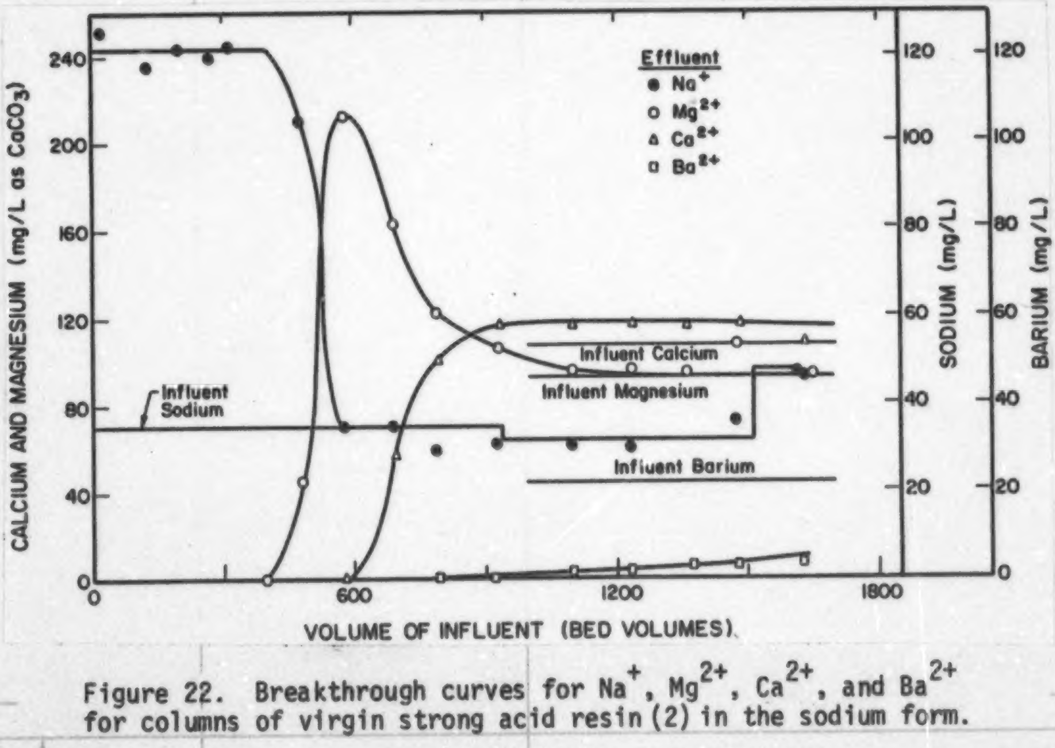

Figure 22. Breakthrough curves for Na$^+$, Mg^{2+}, Ca^{2+}, and Ba^{2+} for columns of virgin strong acid resin (2) in the sodium form.

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Chromatographic displacement of the ions was again observed in the reverse order of their selectivity, with sodium breaking through first, followed by magnesium, then calcium and lastly barium.

The performance of the hydrogen form resin was fairly similar to that obtained from the shorter 11 cm deep column. Magnesium and calcium breakthrough occurred somewhat earlier during the run of the deeper column, possibly because of the much lower sodium during this run. Barium breakthrough of 1.0 mg/L occurred at approximately 1620 BV for the deep column and at approximately 1700 BV for the shorter column. A problem with the pump used on the deeper column occurred for the first 300 BV, which introduced some uncertainty into the calculation of the amount of influent applied.

The performance of the resin column in the sodium form was similar to the 62 cm deep resin column in the hydrogen form with respect to magnesium and calcium breakthrough, but not with respect to barium breakthrough. Barium breakthrough of 1.0 mg/L occurred at approximately 1050 BV for the sodium form compared to approximately 1620 BV for the same resin in the hydrogen form. Part of this difference may be due to pumping difficulties which were encountered with the 62 cm-deep sodium- and hydrogen-form columns. Also, a problem with entrapment of significant amounts of gas bubbles within the sodium form was encountered, and may have led to earlier breakthrough of barium. Because of the difficulties encountered in these runs, no firm conclusions can be made about the merits of using a shallow column vs. a deep column. The deep column was used in all subsequent tests.

The pH of the effluent from the hydrogen form resin column for approximately the first 300 BV was less than 3.5, compared to the sodium form resin column which showed no pH drop. The effluent from the hydrogen form resin column also had zero alkalinity for the first 300 BV, and then it rose very quickly to that of the influent; for the sodium form resin the effluent alkalinity remained unchanged from that of the influent for the entire run. For both the hydrogen and sodium form resin columns, the effluent sodium concentration, peaked at approximately three times the influent concentration, and the effluent magnesium concentration peaked at over two times the influent concentration.

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TABLE 15. CATION REMOVAL BY THE SECOND COLUMN TEST WITH VIRGIN STRONG ACID RESIN

	Strong Acid Resin	
	H^+ Form (meq/g resin)	Na^+ Form (meq/g resin)
Alkalinity neutralized	4.71	N/A
Mineral acidity produced	Large amount, but not measured	N/A
Na^+ adsorbed by resin	1.32	-
Na^+ displaced during run	0.82	5.28
Na^+ on resin at termination of run	0.50	*
Mg^{2+} adsorbed by resin	2.14	2.20
Mg^{2+} displaced during run	1.30	1.58
Mg^{2+} on resin at termination of run	0.84	0.62
Ca^{2+} adsorbed by resin	3.62	3.89
Ca^{2+} displaced during run	0.78	0.42
Ca^{2+} on resin at termination of run	2.84	3.47
Ba^{2+} adsorbed by resin	1.22	1.12
Total capacity utilized during column runs	5.40	5.20 - 5.28
Manufacturer's minimum capacity	5.0	5.0

*Not measured.

Shown in Table 15 is a summary of the quantities of ions removed from the influent solution during exhaustions of the columns. The total capacity utilized of the resins was close to the manufacturer's stated minimum capacity for the resin.

The saturated resin columns were regenerated under the following conditions:

Hydrogen Form Column

8% hydrochloric acid solution (2.26 eq/L)

Regenerant applied: 18.6 lb HCl/ft^3 resin (3.66 BV; 21.7 meq/g)

Application rate: 8.15 mL/min (0.41 gpm/ft^2; 1.64 BV/hr)

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Sodium Form Column

13.5% sodium chloride solution (2.54 eq/L)

Regenerant applied: 29.9 lb NaCl/ft^3 resin (3.23 BV; 21.7 meq/g)

Application rate: 8.12 mL/min (0.40 gpm/ft^2; 1.64 BV/hr)

The regeneration of each column was performed upflow, co-current to the direction of flow during the exhaustion run. The resin remained firmly packed in the columns at all times, however. Effluent samples were taken continuously throughout regeneration and analyzed for magnesium, calcium, and barium; the HCl regeneration curves for the acid form of the resin are shown in Figure 23.

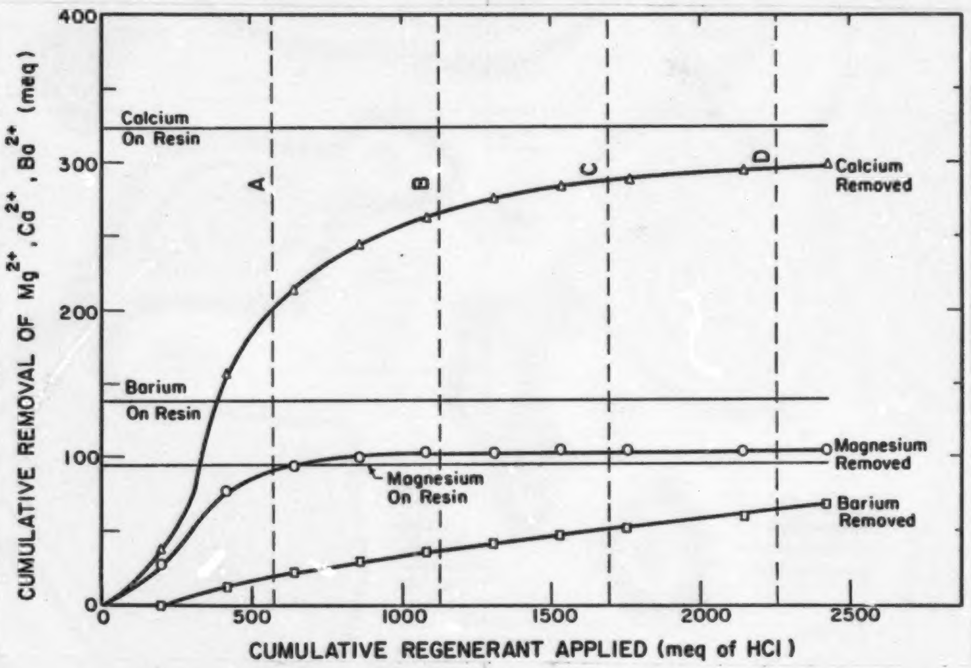

Figure 23. Acid regeneration of virgin strong acid resin (2). At A, B, C and D, respectively, the amount of regenerant applied is 1, 2, 3 and 4 times the number of equivalents of cations removed by the resin.

The curves show the cumulative metal ion removal as a function of the amount of regenerant applied. Calcium and magnesium are removed most effectively during the first portion of the regeneration. At a regenerant dose equivalent to the resin capacity (at line A), 55 percent of all ions were

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removed (based on the total amount eventually removed from the resin during regeneration), 80 percent of the magnesium and 67 percent of the calcium were removed. Barium was the most difficult ion to remove, as also was found during the regeneration of the hydrogen form resin column during the first column study. Only 15 percent of the barium ions were removed by this amount of regenerant, however. After an amount of regenerant equal to three times the equivalents of divalent cations removed (line C) was applied, essentially all of the calcium and magnesium were removed from the resin - but more than 50 percent of the barium remained on the resin.

The regeneration curves for the sodium chloride regeneration of the column originally in the salt form are very similar to those obtained for the hydrochloric acid regeneration and thus they are not shown. No difference in the regeneration ability of the hydrochloric acid versus sodium chloride was observed.

A large regenerant dose would be required to regain the full capacity of this resin. In municipal softening operations resin capacity is often sacrificed in order to achieve greater regeneration efficiency (Bowers, 1971). Municipalities often operate with a regenerant dose of approximately the capacity of the resin (or the equivalents of divalent ions on the resin) where about 50 percent removal of the ions is obtained according to the results shown in Figure 23. The capacity of the resin available in a subsequent production run is then limited by cations still present on the resin. The results from the two virgin resin column studies also indicate that with only partial regeneration of a resin bed between production runs, as in a municipal softening application, barium will accumulate on the resin. This condition is expected to alter the relative amount of water that can be processed before hardness and barium breakthrough.

D. Weak Acid Virgin Resin Column Studies

1. First Column Study

Two column studies with virgin weak acid resin were performed to examine its hardness and barium breakthrough characteristics. The first column study was carried out until the resin was completely saturated, i.e., until the influent and effluent concentrations were equal. The study was conducted

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using a short column (8.1 cm) of the hydrogen form of the resin. The column had a bed volume of 40 mL measured after saturation of the column. The flow rate of the influent was 0.3 gpm/ft^2 (8.3 BV/hr, or about one-half the rate used in typical full-scale operations) and the influent was pumped upflow through the columns.

The influent solution was the same as the solution used for the first strong acid virgin resin column study. The influent characteristics were:

Na^+	197 mg/L
Mg^{2+}	92 mg/L as $CaCO_3$
Ca^{2+}	109 mg/L as $CaCO_3$
Ba^{2+}	22 mg/L
Total Hardness	201 mg/L as $CaCO_3$
Total Alkalinity	250 mg/L as $CaCO_3$
pH	6.8 - 7.1

The magnesium, calcium, and barium effluent profiles over the course of the run are shown in Figure 24. The breakthrough curves are shown as a function of bed volumes throughput.

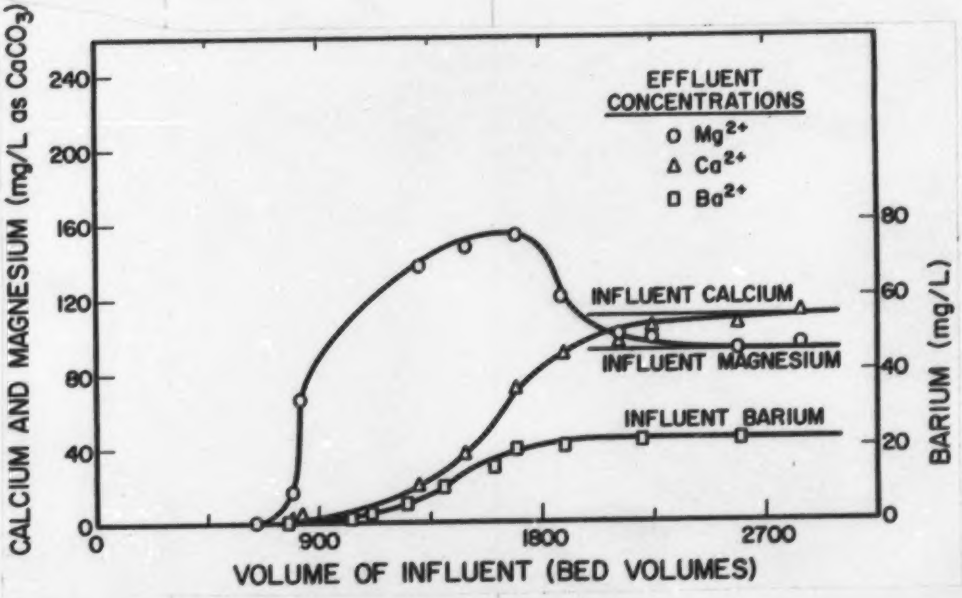

Figure 24. Breakthrough curves for virgin weak acid resin.

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As expected, the cations appeared in the effluent in the reverse order of their selectivity. Magnesium appeared at 650 BV, showing that hardness breakthrough in a softening operation is likely to be governed by magnesium breakthrough.

Calcium and barium appeared in the effluent after 800 BV passed through the column. Their appearance at the same time suggests that the selectivities of barium and calcium over the hydrogen ion are very nearly identical. The barium concentration did not surpass the MCL of 1 mg/L until 975 BV. At a barium concentration of 1 mg/L the total hardness in the effluent was 130 mg/L as $CaCO_3$. Therefore, barium removal should be more than adequate when the weak acid resin is used for complete softening.

The magnesium concentration reached a peak of 160 mg/L as $CaCO_3$ at 1500 BV due to the displacement of magnesium by calcium and barium. Since the weak acid resin has a higher selectivity for calcium and barium, these ions are adsorbed preferentially over magnesium.

TABLE 16. CATION REMOVAL BY THE FIRST COLUMN TEST WITH VIRGIN WEAK ACID RESIN

Alkalinity neutralized	4.64 meq/mL
Mineral acidity produced	Small but not measured
Mg^{2+} adsorbed by resin	1.55 meq/mL
Mg^{2+} displaced	1.00 meq/mL
Mg^{2+} on resin at termination	0.55 meq/mL
Ca^{2+} adsorbed by resin	3.55 meq/mL
Ba^{2+} adsorbed by resin	0.49 meq/mL

Table 16 shows the total ions adsorbed and remaining on the resin column at the end of the first column run. Values are given in volume capacities as opposed to weight capacities since the weight of the resin was not measured prior to the column run. The total quantity of ions remaining on the resin was 4.59 meq/mL and can be considered the saturation capacity of the resin. This agrees well with the 4.64 meq/mL of alkalinity neutralized during the run. When the alkalinity in the effluent is equal to the alkalinity of the influent, the resin is no longer exchanging hydrogen ion. The column then is completely saturated with metal ions and the quantity of metal ions adsorbed should equal the amount of alkalinity neutralized.

Once the column is at equilibrium with the influent concentrations, selectivity coefficients can be determined.

$$K_{Ca}^{Mg} = \frac{\overline{X}_{Mg}^{\,|Z^{Ca}|}\; X_{Ca}^{\,|Z^{Mg}|}}{\overline{X}_{Ca}^{\,|Z^{Mg}|}\; X_{Mg}^{\,|Z^{Ca}|}} = 0.036$$

$$K_{Ca}^{Ba} = \frac{\overline{X}_{Ba}^{\,|Z^{Ca}|}\; X_{Ca}^{\,|Z^{Ba}|}}{X_{Ba}^{\,|Z^{Ca}|}\; \overline{X}_{Ca}^{\,|Z^{Ba}|}} = 0.900$$

where $\overline{X}_{Mg}$, $\overline{X}_{Ca}$, and $\overline{X}_{Ba}$ are the equivalent fraction of Mg^{2+}, Ca^{2+}, and Ba^{2+}, respectively, on the resin. These numbers were obtained by dividing the meq/mL of cation remaining on the resin (see Table 16) by the total capacity. The values X_{Mg}, X_{Ca}, and X_{Ba} are the equivalent fraction of the cations in solution (final concentration of cation divided by the sum of all cation concentrations in solution). The Z^{Ca}, Z^{Ba}, and Z^{Mg} are the valencies of the cations. The above selectivities show that calcium is slightly preferred over barium and strongly preferred over magnesium.

The performance of the weak acid (Duolite C-433) and the strong acid resin (Duolite C-20) for barium and hardness removal are compared in Figure 25. The hardness and barium curves were taken from Figure 24 for the weak acid virgin resin. The strong acid resin data were taken from Figure 16. The hardness was determined by summing the magnesium and calcium concentrations.

The two virgin resins initially in the hydrogen form show significantly different capacities for hardness removal. In a normal municipal softening operation, a column run probably would be terminated at a hardness breakthrough of 40 mg/L as $CaCO_3$. This occurs at 475 BV for the strong acid resin, whereas the same breakthrough occurs at 825 BV for the weak acid column. The weak acid resin has a 1.7 times higher capacity for metal ions than does the strong acid resin at breakthrough.

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Figure 25 also shows the difference in the barium breakthrough curves for the two resin columns. Although the strong acid resin has a considerably lower capacity, the barium breakthrough occurs considerably later than it does for the weak acid resin. The strong acid resin has a much higher affinity for barium ions compared to hardness ions than does the weak acid resin. This greater preference for barium makes the strong acid resin more difficult to regenerate.

Figure 26 shows the alkalinity and hardness effluent profiles for the same two column tests compared in Figure 25. Both runs were made with the resin initially in the hydrogen form. It is important to notice the sharpness of the hardness and alkalinity breakthrough curves for the strong acid resin column. Complete alkalinity breakthrough occurs over a small range of about 25 BV, whereas with the weak acid resin, alkalinity first appears in the influent at 300 BV and complete alkalinity breakthrough does not occur until 1800 BV. The longer time for alkalinity breakthrough is a result of two basic differences between the strong acid and weak acid resins.

The first reason is the strong acid resin's much higher affinity for metal ions than for hydrogen ions. High selectivity results in sharper breakthrough curves. The second reason for the broad peaks is the slow exchange kinetics for the weak acid resin. The kinetics of swelling and dissociation of the hydrogen ion from the carboxylic group are much slower than the steps involved in uptake of ions by strong acid resins. Because the hardness breakthrough curve for the weak acid resin is less steep, a greater percentage of the weak acid column compared to the strong acid column is left unused when the run is terminated.

2. Second Weak Acid Virgin Resin Column Study

The influent solution to the second column contained:

Na^+	35 mg/L
Mg^{2+}	90 mg/L as $CaCO_3$
Ca^{2+}	103 mg/L as $CaCO_3$
Ba^{2+}	19 mg/L
Total Hardness	193 mg/L as $CaCO_3$
Total Alkalinity	250 mg/L as $CaCO_3$
pH	6.9 - 7.3

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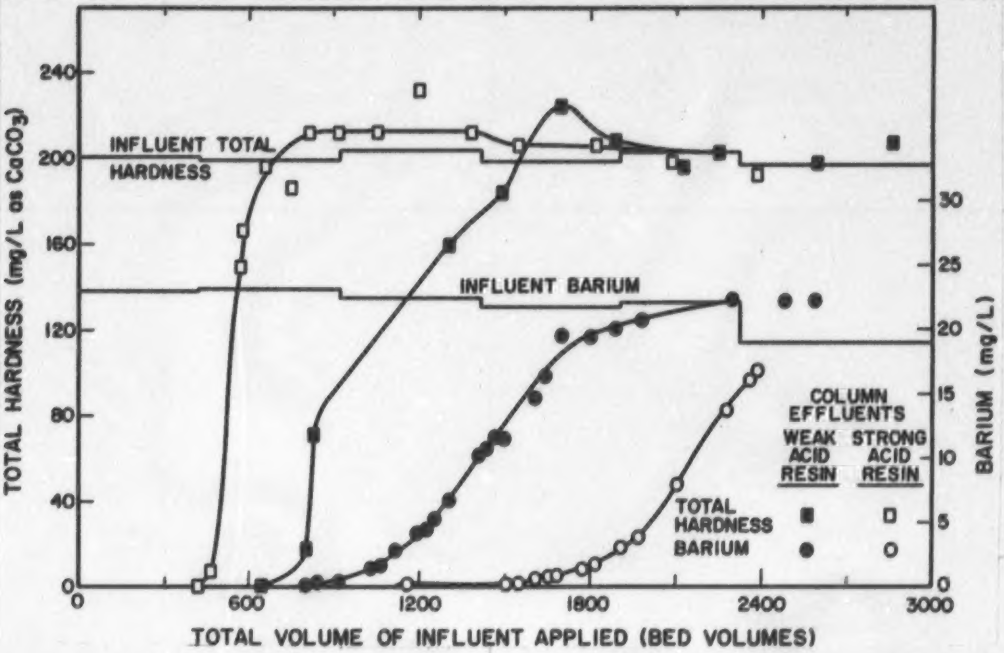

Figure 25. Weak acid vs. strong acid virgin resin breakthrough curves for hardness and Ba^{2+}.

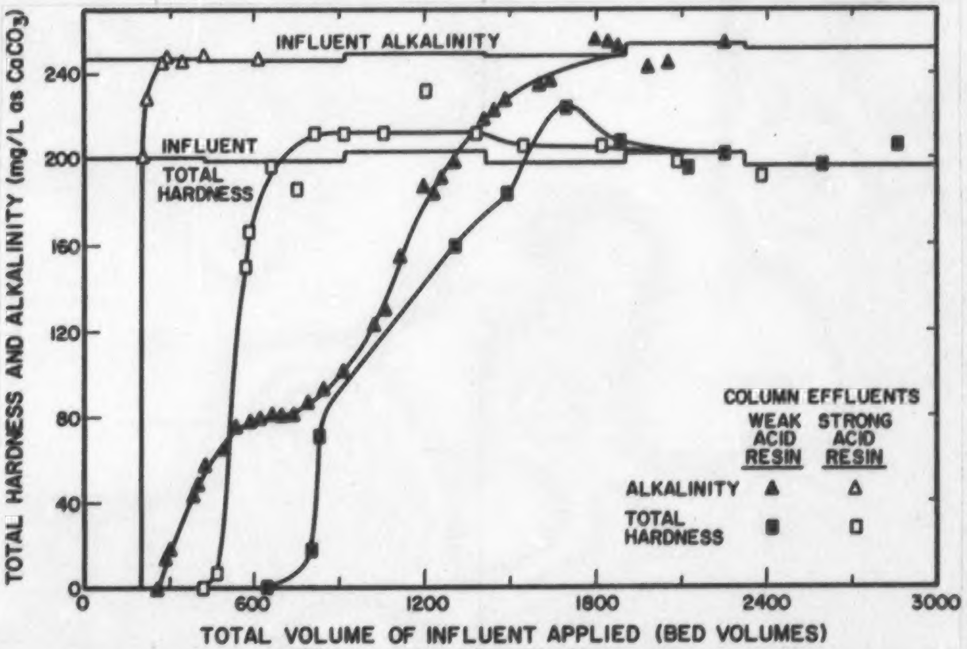

Figure 26. Weak acid vs. strong acid virgin resin breakthrough curves for hardness and alkalinity.

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The column contained 61.6 cm of resin which is typical of column lengths used in practice. The volume of the bed was 297 cm^3. The flow rate initially was 1.3 gpm/ft^2 (5.1 BV/hr) but after 366 BV, pump difficulties caused the flow rate for the rest of the run to be 0.65 gpm/ft^2 (2.6 BV/hr). The test was terminated before complete alkalinity breakthrough at about 1170 BV (at 1 mg/L Ba^{2+} breakthrough).

The breakthrough profiles are very similar to those found in column test #1 (Figure 24) and thus are not shown. Table 17 shows the total ions adsorbed in meq/mL and meq/g. The values given in meq/mL can be compared with results from column test #1. The 3.74 meq/mL of alkalinity neutralized in column test #2 is less than 4.64 meq/mL neutralized in column test #1 because test #2 was not run to complete alkalinity breakthrough. Thus, about 20 percent of the resin in the column was still in the hydrogen form at the termination of the run.

The total quantity of metal ions adsorbed (4.04 meq/mL) does not agree with the quantity of alkalinity neutralized as it did for test #1. The difference is probably attributable to analytical error.

TABLE 17. CATION REMOVAL BY THE SECOND COLUMN TEST WITH VIRGIN WEAK ACID RESIN

	meq/mL (H^+ form)	meq/g (H^+ form)
Alkalinity neutralized	3.74	9.62
Mg^{2+} adsorbed by resin	1.51	3.88
Mg^{2+} displaced during run	0.33	0.84
Mg^{2+} on resin at termination of run	1.18	3.04
Ca^{2+} adsorbed by resin	2.56	6.57
Ba^{2+} adsorbed by resin	0.30	0.78
Total ions on resin at termination of run	4.04 meq/mL	10.39 meq/g

An important comparison to make between strong acid sodium form columns and weak acid hydrogen form columns is the sodium concentration in the column effluent. Figure 27 shows the sodium effluent profiles for weak acid test #2 and a similar strong acid sodium form column test.

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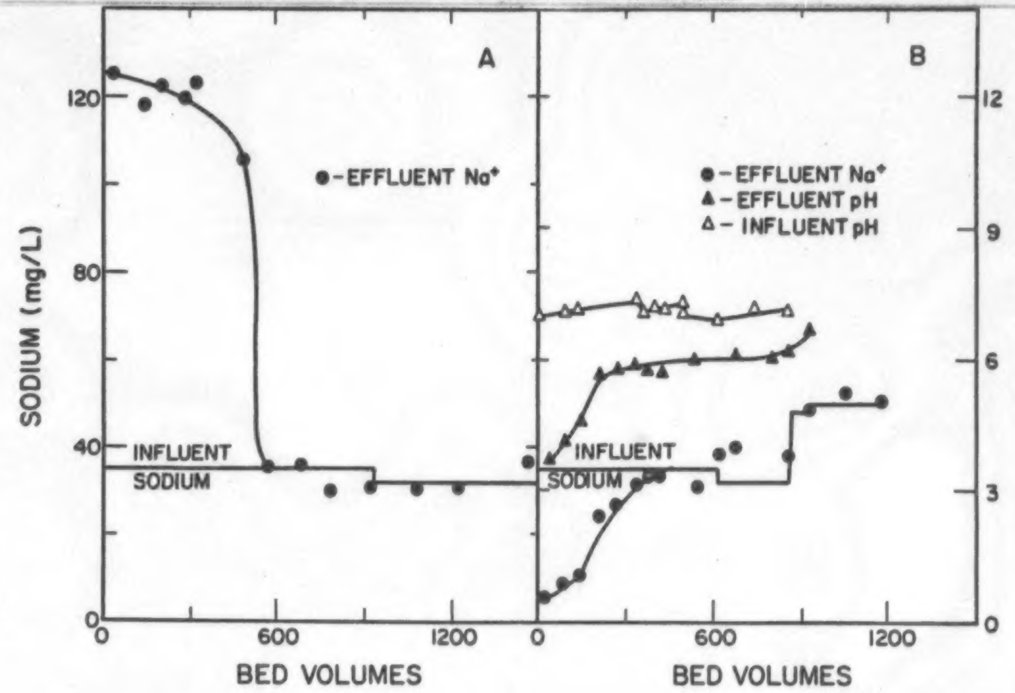

Figure 27. Sodium effluent concentrations for strong acid resin in the sodium form vs. weak acid resin in the hydrogen form.

The sodium in the strong acid effluent reached a maximum of 122 mg/L and was significantly in excess of the influent concentration of 35 mg/L for the first 500 BV, until hardness breakthrough occurred (Figure 27a). Over the course of a softening cycle for this set of influent conditions the average effluent sodium level was 118 mg/L. The weak acid sodium effluent profile was shown in Figure 27b. Sodium appeared immediately in the effluent and rose slowly over the next 450 BV. A mass balance on sodium showed that only about 5 percent of the sodium adsorbed remained on the column just before regeneration. Therefore, the average sodium effluent concentration was approximately equal to the influent concentration for the weak acid column run.

Also shown in Figure 27b is the influent and effluent pH levels for the weak acid column test. Over the course of the column run the pH of the effluent ranged from 3.7 to 6.7. This is considerably lower than is acceptable for a distribution system. After the carbon dioxide is stripped by aeration following ion exchange, the pH can be raised with only a small addition of sodium hydroxide. Most conventional stripping towers reduce the car-

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bon dioxide to 10 mg/L or less. Sodium hydroxide can then be used to raise the pH to 8.3 while only adding 7 to 10 mg/L of sodium. Thus, even when sodium hydroxide is added to adjust the pH, the effluent from weak acid cation exchanger contains considerably less sodium than strong acid sodium form cation exchanger.

When the strong acid resin is used in the sodium form the effluent pH is simply equal to the influent pH. It is not inconceivable that the influent pH may be too low and corrosive to water mains. Therefore, the pH may also need to be adjusted in the strong acid resin effluent.

Regenerant was applied to column #2 upflow (co-current); 7.6 BV of a 3.54 percent (0.98 N) HCl solution was used. Regeneration was followed by 6.7 BV of distilled water rinse. Both the regenerant and rinse water were pumped at a flow rate of 6 BV/hr.

Figure 28 shows the cumulative equivalents of magnesium, calcium and barium removed as a function of the equivalents of HCL applied. The horizontal lines represent the equivalents of each metal taken up by the resin, calculated from the difference between column influent and effluent concentrations. The vertical line "A" represents a regenerant dose of 10.4 meq HCl/g of resin, which was equal to the equivalents of divalent cations on the column just prior to regeneration. The vertical line labeled "B" represents a regenerant dose of 15.6 meq HCl/g of resin or a quantity equal to 1.5 times the equivalents of divalent ions on the resin.

As shown in Figure 28, there was a discrepancy in the quantity of calcium and magnesium removed during regeneration and the quantity left on the resin at the end of the exhaustion run. About 0.24 meq/g more magnesium was removed than was thought to be on the column and 0.55 meq/g more calcium was considered to be on the column than was removed. These differences are likely attributable to analytical sensitivity.

If the quantity of ions removed is compared with the total quantity of acid applied it is evident that the regeneration of the weak acid (Duolite C-433) is very efficient. After a regenerant dose of 10.4 meq/g (equal to 1.0 times the equivalents of divalent cations removed) had been applied in the column, 89 percent of the metal ions were removed. Removals of all three

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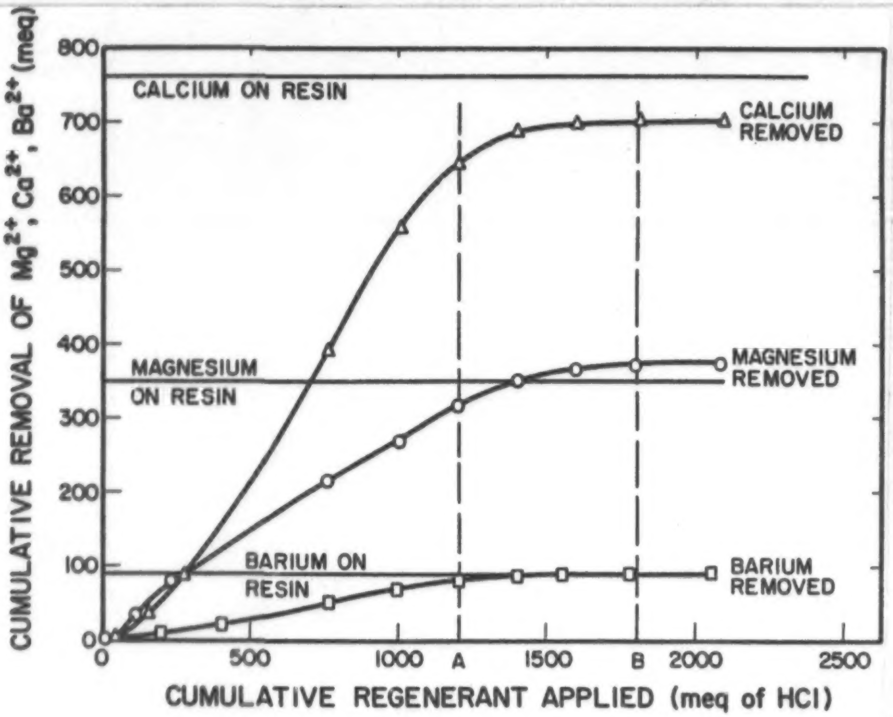

Figure 28. Acid regeneration of virgin weak acid resin (2). At "A" and "B," the equivalents of HCl applied are equal to 1.0 and 1.5 times the divalent cations on the resin, respectively.

ions were nearly the same with 84 percent of the magnesium, 92 percent of the calcium and 87 percent of the barium being removed. This shows that the selectivity difference between the ions has little effect on the extent of regeneration. After 15.6 meq of HCl/g (1.5 times the equivalents of cations on the resin) had been applied essentially all of the metal ions were removed.

The efficiency of weak acid resin regeneration can be compared with that for strong acid resin in both the hydrogen and sodium forms. When a regenerant dose equivalent to the capacity utilized by divalent ions was applied to a strong acid resin approximately 60 percent of the cations were removed. Regeneration of strong acid resins was also significantly affected by selectivity, because large regenerant doses were required to completely remove the barium.

The fact that barium is removed from the weak acid resin as effectively as hardness is significant. One would not expect any selective barium accumulation on the resin in the event that the resin was not completely

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regenerated before reuse. Also the relative times for hardness and barium breakthrough should not change over many exhaustion-regeneration cycles.

E. Strong Acid Resin Exhaustion-Regeneration Cyclic Column Studies

Two strong acid resin columns, one in the sodium form and the other in the hydrogen form, were operated through repeated exhaustion-regeneration cycles in order to simulate the use of the resin in practice. The exhaustion portion of each cycle was terminated when approximately 40 mg/L of total hardness (as $CaCO_3$) was observed in the column effluent. The resin was then regenerated, rinsed, and the cycle was then repeated.

The cyclic column studies were conducted in order to determine if barium would accumulate on the resin with successive cycles, thereby changing the relative breakthrough time of total hardness and barium. They were also intended to yield information on the working capacity of the resin, to show whether amounts of regenerant in excess of that typically used would be required in order to hold the barium concentration as hardness breakthrough below an acceptable level, to document the extent of leakage during the duration of a column run, and to determine whether the BV processed per cycle would change with the number of cycles.

Two 2.5 cm diameter columns were filled with 63 cm of resin. At the top of each resin bed, approximately 5 cm of free space was left to allow a slight backwash expansion of each bed before each regeneration. One column filled with resin was converted to the sodium form by pumping 3.07 L of a 13.5 percent sodium chloride solution through the column at 1.89 BV/hr, followed by 1.1 L of distilled deionized rinse water at 2.07 BV/hr.

The experimental parameters for the two columns were:

Hydrogen Form Column

2.48 cm diameter, 63.2 cm depth
114.7 g resin (dry weight, hydrogen form)
1 bed volume = 304.2 mL (wet volume, hydrogen form)
Influent applied at: 86.4 mL/min (4.4 gpm/ft^2; 17.1 BV/hr)

Sodium Form Column

2.48 cm diameter, 62.9 cm depth
114.2 g resin (dry weight, hydrogen form)

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1 bed volume = 302.8 mL (wet volume, hydrogen form)

Influent applied at: 86.5 mL/min (4.5 gpm/ft^2; 17.1 BV/hr)

The flow rates were within the range of rates used in practice. The influent batches were prepared in a 230 gallon stainless steel covered tank. The average influent composition for the cyclic column studies was:

Na^+	38.7 mg/L
Mg^{2+}	102.2 mg/L as $CaCO_3$
Ca^{2+}	102.2 mg/L as $CaCO_3$
Ba^{2+}	19.8 mg/L
^{226}Ra	19.1 pCi/L
Total Hardness	204.4 mg/L as $CaCO_3$
Total Alkalinity	251.5 mg/L as $CaCO_3$
pH	6.5 - 7.2

Influent was pumped, by a separate pump for each column, downflow through the resin beds. Effluent samples were taken at a frequency dependent on the effluent concentration and analyzed immediately for total hardness by EDTA titration. Several effluent samples were taken near the end of each exhaustion cycle in order to determine the barium and radium^{226} concentrations when the total hardness reached 40 mg/L as $CaCO_3$. From two of the cycles of the sodium form column, effluent samples were taken throughout the run in order to determine extent of leakage. All influent and effluent samples were analyzed for magnesium, calcium, and barium. One-liter samples of the influent and effluent from some of the cycles of the sodium form column were taken in polyethylene bottles and analyzed for radium^{226}.

Prior to each regeneration, each column was backwashed for 2 to 3 minutes with distilled deionized water to expand the resin bed about 5 cm. The saturated resin columns were then regenerated co-current to the direction of flow during the exhaustion portion of the cycle, under the following average conditions:

Hydrogen Form Column

8% Hydrochloric acid solution (2.255 eq/L)

Regenerant applied:

For cycles 1 to 3: 4.61 lb HCl/ft^3 resin

(0.90 BV; 5.37 meq HCl/g)

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For cycles 4 to 5: 4.06 lb HCl/ft^3 resin

(0.79 BV; 4.72 meq HCl/g)

Application rate: 8.56 mL/min (0.44 gpm/ft^2; 1.7 BV/hr)

Rinse water applied: 5.6 BV

Slow rinse rate: 1.7 BV/hr for 44 min

Fast rinse rate: 7-8 BV/hr for 33 min

Sodium Form Column

13.5% Sodium chloride solution (2.54 eq/L)

Regenerant applied:

For cycles 1 to 11: 6.5 lb NaCl/ft^3 resin

(0.702 BV; 4.72 meq NaCl/g)

For cycles 12 to 19: 9.75 lb NaCl/ft^3 resin

(1.053 BV; 7.09 meq NaCl/g)

Application rate: 8.53 mL/min (0.44 gpm/ft^2; 1.7 BV/hr)

Rinse water applied: 5.3 BV

Slow rinse rate: 1.7 BV/hr for 48 min

Fast rinse rate: 7-8 BV/hr for 26 min

The regenerant dose of 4.61 lb HCl/ft^3 of resin used for the three cycles of the hydrogen form resin column was chosen based on the assumption that hydrogen ions would be less efficient than sodium ions in regenerating the resin - based on the higher selectivity of the resin for Na$^+$ over H$^+$ (4.61 lb HCl/ft^3 resin would provide the same extent of regeneration as 6.5 lb NaCl/ft^3 of resin assuming HCl is 44 percent efficient at regenerating and NaCl is 50 percent efficient). Regeneration efficiency is a measure of how easily metal ions can be removed from an ion exchange column. Regeneration efficiency is determined by:

$$\frac{\text{Total equivalents of metal ions removed during regeneration}}{\text{Total equivalents of H}^+(\text{Na}^+)\text{ ions applied during regeneration}} \times 100\%$$

The barium concentration in the effluent at the end of the first three cycles of the hydrogen form resin column was increasing at a slightly slower rate than that for the sodium form resin column. This indicated that the extra HCl used was removing additional metals during regeneration than was being removed by the 6.5 lb NaCl/ft^3.

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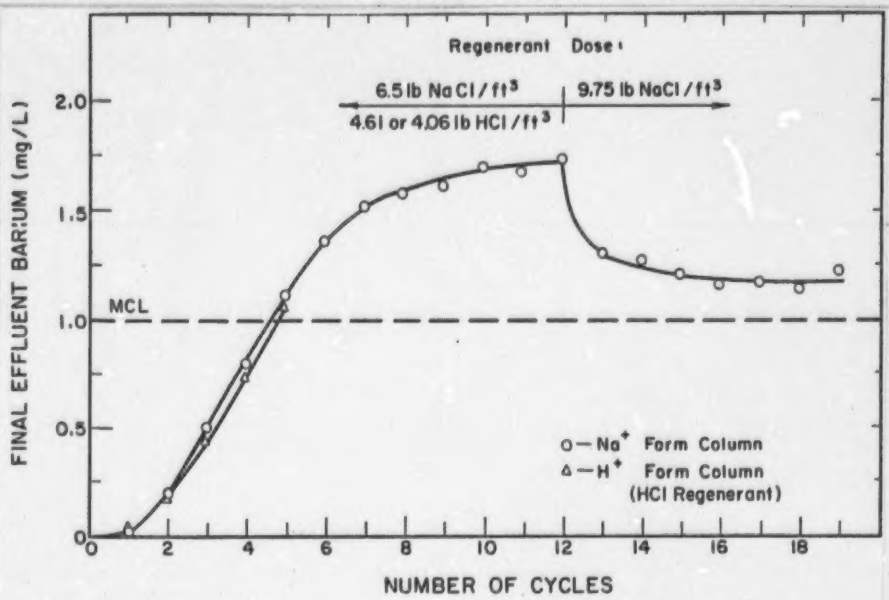

Figure 29. Barium effluent concentration from strong acid resin exhaustion-regeneration cyclic studies. The barium values shown are those when the effluent hardness concentration is 40 mg/L as $CaCO_3$.

For the last two cycles of the hydrogen form resin column the regenerant dose was decreased to 4.06 lb HCl/ft^3 of resin (4.72 meq/g) which yields the same number of equivalents per regeneration as 6.50 lb NaCl/ft^3. The barium concentration in the effluent from the hydrogen form column at the end of the last two cycles was approaching that obtained from the 6.50 lb NaCl/ft^3 of resin. These results indicate that there is very little, if any, difference in the regeneration efficiencies of sodium chloride solution and hydrochloric acid solution. The operation of the hydrogen form column was discontinued, as it was yielding results quite similar to those of the sodium form column.

The final effluent barium concentrations, when 40 mg/L of total hardness (as $CaCO_3$) was present in the effluent, of both the sodium and hydrogen form resin columns are shown in Figure 29. The effluent barium concentration leveled off at 1.7 to 1.75 mg/L for the cycles where 6.5 lb NaCl/ft^3 of resin was used for the regeneration of the sodium form resin column. A mass balance on Ba^{2+} showed 0.98 meq Ba^{2+}/g resin just before regeneration in the 11th cycle, and 0.81 meq/g after regeneration. The effluent barium concentration dropped to about 1.2 mg/L at the end of each cycle after the regenerant dose

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was increased by 50 percent to 9.75 lb NaCl/ft^3 of resin. By the 19th cycle, 0.86 meq Ba^{2+}/g was on the resin before regeneration, and 0.62 meq/g remained after regeneration.

The results shown in Figure 29 indicate that barium does accumulate on the resin with successive exhaustion-regeneration cycles. This accumulation levels off at a concentration dependent on the total hardness concentration at which the run is terminated, and on the amount of regenerant applied for each regeneration. In the 10th and 11th cycles of the sodium form of the resin, for example, the divalent cation removal was 2.77 meq/g resin, which is about 58 percent of the maximum capacity of the resin. A large portion of the remaining 42 percent of the maximum capacity was occupied by ions that were not removed by the regenerant.

The regeneration efficiency (equivalents removed per equivalent of regenerant applied), obtained for the 10th and 11th cycles with 6.50 lb NaCl/ft^3 of resin was 58-59 percent. The average TDS of the 2.4 BV of waste brine produced per 100 BV of product water was 16,400 mg/L. The waste brine figure does not include the backwash water which would be used to backwash the resin beds for each regeneration but does include the rinse water. No effort was made to minimize the volume of brine produced.

The regeneration efficiency obtained for the 17th, 18th, and 19th cycles, with application of 9.75 lb NaCl/ft^3 of resin, was 46.0 percent. The waste brine produced was 2.07 BV per 100 BVs of product water; the average TDS of the brine was 25,200 mg/L. The capacity used during these cycles was 3.26 meq/g, or 67.9 percent of the maximum capacity.

For the 4th and 5th cycles of the hydrogen form resin column, which used 2.98 meq/g of capacity (62.1 percent of maximum capacity), the regenerant dose was 4.06 lb HCl/ft^3 of resin and the regeneration efficiency obtained was 63.0 percent. The waste brine produced was 2.2 BV per 100 BVs of product water with an average TDS of 14,000 mg/L. After neutralizing the product water to pH 7.0 with 0.039 BV of 6.0 N NaOH per 100 BV water, 2.23 BV of spent brine resulted per 100 BV water with an average TDS of 16,000 mg/L.

The breakthrough curves shown in Figure 30 were determined during the 6th exhaustion of the sodium form resin column, with 6.50 lb NaCl/ft^3 of resin

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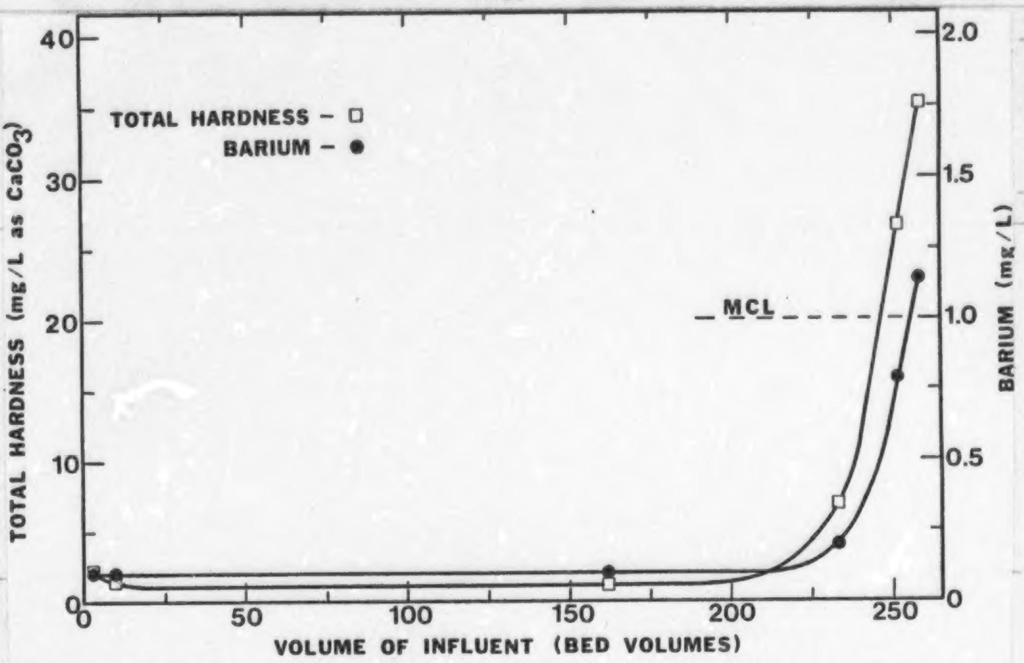

Figure 30. Breakthrough curves for the sixth exhaustion cycle of the strong acid resin.

applied as regenerant. The leakage of barium during most of the cycles was very low, approximately 0.10 mg/L, including at the beginning of the run. Very low total hardness leakage was also observed for this cycle. Barium and total hardness broke through together at approximately 225 BV. Effluent samples taken during the 9th, 10th, and 11th cycles of this column continued to show leakage of less than about 0.15 mg/L of barium during most of each cycle.

The breakthrough curves determined during the 19th cycle of the sodium form resin column, with a regenerant dose of 9.75 lb NaCl/ft^3 of resin, were very similar to those shown in Figure 30. The leakage of barium was between 0.10 mg/L and 0.20 mg/L for the entire run. Hardness and barium did breakthrough somewhat later at 260 to 270 BV, however, in keeping with the usage of a higher percentage of the resin capacity.

The leakage shown in Figure 30 indicates that the barium remaining on the resin after the completion of the regeneration/rinse portion of the cycle is tightly held by the resin. The barium is not easily displaced by the high

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concentration of Na^+ released in the subsequent saturation cycle as hardness is removed from the influent.

F. Weak Acid Resin Exhaustion-Regeneration Cyclic Column Studies

Three sets of exhaustion-regeneration cyclic tests were performed using a 60.6 cm weak acid resin column. A column was constructed for these tests using a new batch of resin and the same column was used throughout. The column parameters and influent characteristics are given in Table 18.

TABLE 18. EXPERIMENTAL PARAMETERS FOR THE CYCLIC TESTS WITH WEAK ACID RESIN

	Test #1	Test #2	Test #3
Column length (cm)	60.6	60.6	60.6
Column diameter (cm)	2.5	2.5	2.5
Flow rate (gpm/ft^2; BV/hr)	4.3; 17.5	4.0; 16.4	4.1; 16.5
One bed volume (cm^3; g dry weight)	292; 110.7	292; 110.7	292; 110.7
Na^+ (mg/L)	24	51	25
Mg^{2+} (mg/L as $CaCO_3$)	92	98	100
Ca^{2+} (mg/L as $CaCO_3$)	97	102	98
Ba^{2+} (mg/L)	19	20	22
Total hardness (mg/L as $CaCO_3$)	195	200	198
Total alkalinity (mg/L as $CaCO_3$)	250	250	250
pH	6.8 - 7.0	6.8 - 7.0	6.8 - 7.0

Flow rates ranged from 16.4-17.5 BV/hr; these are more representative of flow rates used in practice than the flow rates used in the column tests with virgin resin. The influent characteristics given are averages over each set of tests.

Cyclic Test #1

In cyclic test #1 a set of nine exhaustion-regeneration cycles were performed. The exhaustion part of the cycle was terminated at hardness concentrations ranging from 41.7 to 68 mg/L as $CaCO_3$. Magnesium was the first of the hardness ions to breakthrough. Two different regenerant doses also were used. Over the first five cycles 10.4 meq HCl/g (3.63 BV, 3.95 percent HCl)

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was applied. This dose was chosen based on the results of the virgin column tests. After examination of the regeneration efficiency data it was determined that all of the ions were being removed and that a lower regenerant dose could be applied for a more efficient operation. The regenerant level was reduced for the last four cycles to 9.0 meq/g and was applied as 3.40 BV of 3.58 percent HCl (0.99 N).

The breakthrough capacity, which is defined as the total equivalents of ions adsorbed, and remaining on the resin, prior to the termination of the exhaustion run, varied from 7.9 meq/g to 8.9 meq/g over the nine cycles. No definite upward or downward trend in capacity was observed. Some variation in capacity could have been caused by variation in column operating conditions such as changes in flow rates, and the hardness concentration at which the run was terminated.

The mean capacity was about 8.2 meq/g over the course of cyclic test #1. This capacity is considerably lower than the capacity utilized in column test number two with virgin resin. Due to the earlier termination of these column runs a considerable portion of the resin was left in the hydrogen form.

The percent column utilization is a measure of the capacity utilized and is given by the following equation:

$$\frac{\text{Breakthrough capacity (meq/g)}}{\text{Maximum capacity (meq/g)}} = 100\%$$

The maximum capacity was determined for the Duolite C-433 weak acid resin to be 11.5 meq/g as discussed above.

In cyclic test #1, column utilization varied from 69 to 77 percent with an average of 71 percent. The percentage of resin utilized is a function of the exchange kinetics and regeneration efficiency. The column capacity that was not utilized in the weak acid column remained in the hydrogen form, and thus the observed column utilization was attributable to the kinetics of exchange of divalent cations with the H^+ ions. By comparison, the column utilization for the strong acid could be attributed to the divalent cations that were not removed from the resin during regeneration, as discussed above.

In the first five cycles of cyclic test #1 regeneration efficiency varied from 79 percent to 80 percent when 10.4 meq HCl/g were used. These

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relatively low values were caused by applying more regenerant than was necessary. After lowering the regenerant dose to 9.0 meq HCl/g of resin, the efficiency of regeneration increased to an average of 91 percent over the last four cycles.

For all nine cycles, the barium concentration did not exceed 0.1 to 0.4 mg/L at the time the exhaustion run was terminated. The pertinent data and results of cyclic test #1 are listed in Table 19.

TABLE 19. WEAK ACID EXHAUSTION-REGENERATION CYCLIC TEST #1

Cycle	Breakthrough Capacity (meq/g)	Column Utilization[a] %	Regeneration Efficiency[b,c] %	Terminal Hardness[d] (mg/L as $CaCO_3$)	Terminal Barium (mg/L)
1	8.9	77	79	41	0.2
2	8.4	73	76	60	0.2
3	8.4	73	81	42	0.1
4	8.8	77	88	68	0.1
5	8.0	70	79	54	0.4
6	7.9	69	88	44	0.1
7	8.2	71	91	47	0.3
8	8.0	70	91	42	0.2
9	8.3	72	95	47	0.2

[a] Maximum capacity: 11.5 meq/g

[b] Regenerant applied in cycles 1-5: 10.4 meq/g

[c] Regenerant applied in cycles 6-9: 9.0 meq/g

[d] Hardness is all magnesium

After the ninth exhaustion-regeneration cycle was completed, an additional 5.2 meq HCl/g of resin was applied (1.71 bed volumes of 3.58 percent (0.99 N)) to remove any ions that remained on the resin. The total mass of magnesium, calcium, and barium removed during this final regeneration is listed in Table 20. After a cumulative total of 74.6 meq/g of metal ions were

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adsorbed over the nine cycles, only 0.13 percent (0.1 meq/g) remained after the last cycle. This shows that with a regenerant dose about 10 percent higher than the capacity utilized by divalent ions, the weak acid resin can be regenerated to essentially virgin capacity.

TABLE 20. IONS REMAINING ON THE WEAK ACID RESIN AFTER THE FINAL REGENERATION OF CYCLIC TEST #1

Mg^{2+} removed	0.06 meq/g
Ca^{2+} removed	0.03 meq/g
Ba^{2+} removed	0.007 meq/g

Cyclic Test #2

In cyclic test #2 with the weak acid resin, a set of seven exhaustion-regeneration cycles were performed using a regenerant dose of 7.6 meq HCl/g of resin. During regeneration, 3.4 BV of 3.04 percent (0.84 N) HCl was pumped at a flow rate of 6 BV/hr. This regenerant dose was chosen to determine the column performance when some of the metal ions were not removed from the column during regeneration. Results of the first six column runs are listed in Table 21.

TABLE 21. WEAK ACID EXHAUSTION-REGENERATION CYCLIC TEST #2

Cycle	Breakthrough Capacity (meq/g)	Column Utilization[a] %	Regeneration Efficiency[b] %	Terminal Hardness (mg/L as $CaCO_3$)	Terminal Barium (mg/L)
1	8.7	75	105	51	0.5
2	7.8	68	103	47	0.8
3	7.8	68	101	77	1.1
4	7.6	66	101	70	1.6
5	7.4	64	101	50	1.3
6	7.4	64	102	40	1.3

[a] Maximum capacity: 11.5 meq/g

[b] Regenerant applied: 7.6 meq HCl/g

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The breakthrough capacity decreased sharply between the first and second run. The column was incompletely regenerated after the first exhaustion run and thus the resin still contained some metal ions at the start of the second exhaustion run. This incomplete regeneration also resulted in a decrease in the percent column utilization (from 75 percent to an average of 66 percent), an increase in regeneration efficiency to approximately 100 percent, and in increased Ba^{2+} leakage at the start and end of the exhaustion run.

The removal efficiency of metal ions during regeneration averaged 102 percent over the six exhaustion-regeneration cycles. Efficiencies greater than 100 percent are impossible since the equivalents of metal ions removed can at most equal the equivalents of hydrogen ion applied if all removal is by the exchange mechanism. Values above 100 percent are probably caused by analytical error. However, a reasonable conclusion is that regeneration efficiencies will be very near 100 percent if the column is left about 5 percent saturated after regeneration.

The final barium concentration in the effluent at breakthrough ranged from 0.5 to 1.6 mg/L over the six column runs. The barium concentration increased as the number of cycles increased. The effluent concentration at breakthrough probably was affected by influent concentration, which was about 14.0 mg/L for the first two runs compared to an average of 20 mg/L over all six cycles. The effluent barium concentration appeared to stabilize at a level of 1.3 mg/L by the end of the sixth run. The value of 1.6 mg/L experienced in run four was probably due to the higher hardness concentration (70 mg/L as $CaCO_3$) when the run was terminated.

It is important to recognize that the barium concentration is greater than the MCL of 1.0 mg/L only at the very end of the runs. Thus, if two columns were used in parallel, as is common in practice, the blended water could have a barium concentration of less than 1 mg/L. To achieve this, it would be necessary to regenerate one column while the other is in the middle of its exhaustion cycle.

A seventh column run was also run as a part of cyclic test #2. Whereas the first six column runs were completed at hardness breakthroughs between 40 and 80 mg/L as $CaCO_3$ the seventh column run was carried out to 96 percent saturation with divalent metal ions. Additional samples were collected during cycle seven to examine effluent profiles and determine if there were any notable differences from the virgin column tests.

Results of exhaustion run seven are shown in Figure 31. Effluent profiles for calcium, magnesium and barium are very similar to those found in column test #1 with virgin resin, with the exception that all of the ions appear in the effluent sooner. Magnesium breakthrough occurs at 660 BV as opposed to 825 BV in the column test with virgin resin. This was expected since a portion of the exchange capacity was not available due to incomplete regeneration.

As is evident from Figure 31, there is hardness and barium leakage occurring at the beginning of the column run. Figure 32 is a plot of the barium hardness data from Figure 31 but shown with an expanded scale. Hardness and barium in the effluent at the beginning of the column run were a result of metal ions left on the column after the previous regeneration. Metal ions that are not removed during regeneration will be concentrated at

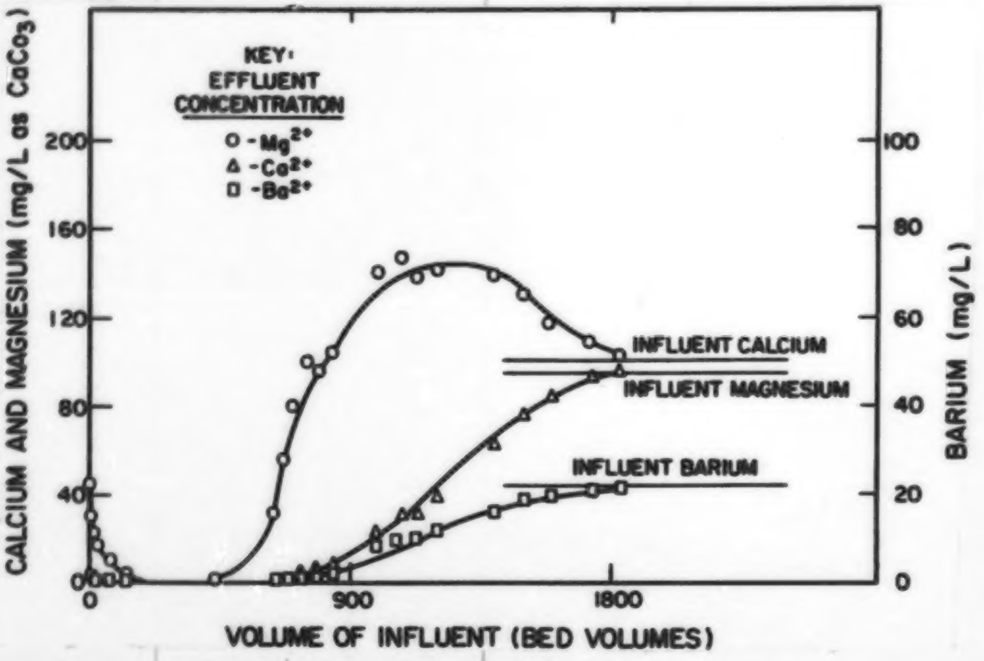

Figure 31. Weak acid resin breakthrough curves for run #7 of cyclic run #2. Regenerant dose was 7.6 meq HCl/g.

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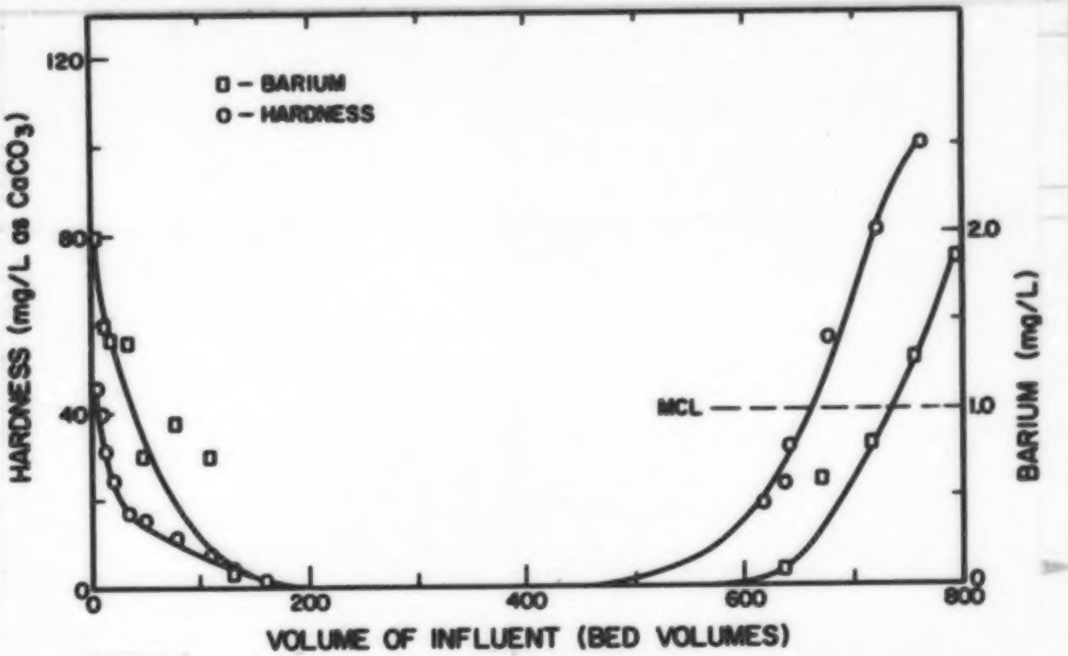

Figure 32. Weak acid resin breakthrough curves for run #7 of cyclic run #2. Regenerant dose was 7.6 meq HCl/g.

the effluent end of the resin column (regenerant solution was applied upflow, co-current to the flow of product water). As the influent enters the column, hardness and barium ions are removed producing carbonic acid. As the low pH carbonic acid solution passes through the remainder of the column some of the metal ions that were not removed during regeneration will be stripped.

The barium leakage at the beginning of the column run is more significant than the barium breakthrough occurring at the end of the run for conditions pertaining to Figure 32. Almost immediately after the column run begins, the barium concentration is 2.0 mg/L. If this water was blended with an equal amount of treated water that contained no barium, the combined effluent would be 1 mg/L. If slightly more barium were left on the resin after regeneration, the quality of product water from a two column system operated in parallel would exceed the MCL.

One possible solution to reducing leakage would be to regenerate in a countercurrent mode. This would leave the metal ions that were not removed during regeneration concentrated at the influent end of column. As the influent passed by these exchange sites little or no stripping would take place because of the higher pH of the water. After column run seven, the weak acid resin column was regenerated with 8.56 BV of 3.04 percent (0.84 N) HCl. The quantity of divalent ions removed was 11.1 meq/g of resin showing that the column was very near complete saturation at 11.5 meq/g.

Cyclic Test #3

Cyclic test #3 consisted of six exhaustion-regeneration cycles that were performed with a regenerant dose of 8.5 meq HCl/g of resin. During regeneration, 3.5 BV of 3.36 percent (0.93 N) HCl were pumped through the column at a flow rate of 6 BV/hr. This regenerant level was chosen to examine the column performance at a level of regenerant intermediate to the previous two doses. The results are listed in Table 22.

TABLE 22. WEAK ACID EXHAUSTION-REGENERATION CYCLIC TEST #3

Cycle	Breakthrough Capacity (meq/g)	Column Utilization[a] %	Regeneration Efficiency[b] %	Terminal Hardness (mg/L as $CaCO_3$)	Terminal Barium (mg/L)
1	8.0	70	95	45	0.2
2	7.8	68	96	42	0.0
3	7.8	68	95	46	0.1
4	7.8	68	96	42	0.1
5	7.8	68	93	38	0.1
6	8.2	71	94	43	0.2

[a] Maximum capacity: 11.5 meq/g

[b] Regenerant applied: 8.5 meq/g

Breakthrough capacities ranged from 7.8 to 8.2 meq/g and column utilization ranged from 68 percent to 71 percent. There was no sharp decrease in breakthrough capacity over the first two runs as in cyclic test #2. This indicates that most of the metal ions were removed during regeneration and near virgin capacity was retained from cycle to cycle.

Regeneration efficiency averaged 95 percent for the six-column run, which was slightly lower than that experienced in cyclic test #2, in keeping with the application of a greater amount of regenerant than metal ions removed. The waste brine volume was 1.2 BV/100 BV of product water with a TDS of 19,900 mg/L.

The effluent barium concentrations ranged from 0 to 0.2 mg/L for hardness concentrations of 46 mg/L as $CaCO_3$ or less. Barium concentrations in this range are at the lower end of the detection limits of ion chromatography, and therefore it was difficult to measure exact concentrations. However, it is safe to conclude that barium removal is more than acceptable for this set of runs.

Hardness and barium concentration profiles are shown in Figure 33 for the sixth exhaustion run of cyclic test #3. There was only minor hardness and barium leakage at both the beginning and end of the run; thus it appears that a still lower regenerant dose, perhaps 8.0 meq HCl/g, would give satisfactory performance.

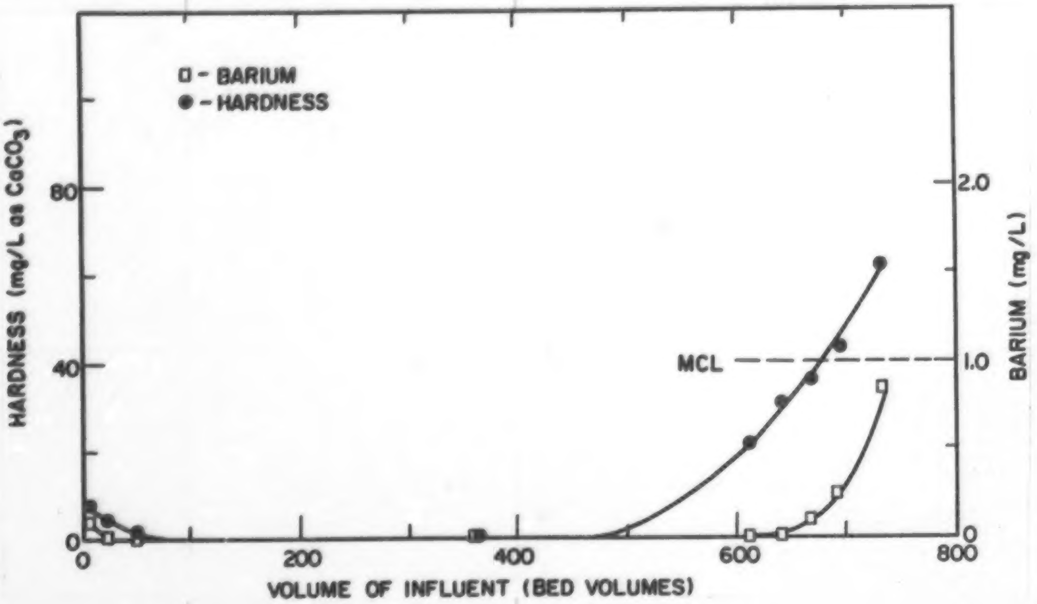

Figure 33. Weak acid resin breakthrough curves for run #6 of cyclic run #3. Regenerant dose was 8.5 meq HCl/g.

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The barium removal performance of each of the cyclic tests is summarized in Figure 34. The final barium concentrations are plotted for the last four runs of cyclic test #1 and for the first six runs each of cyclic tests #2 and #3.

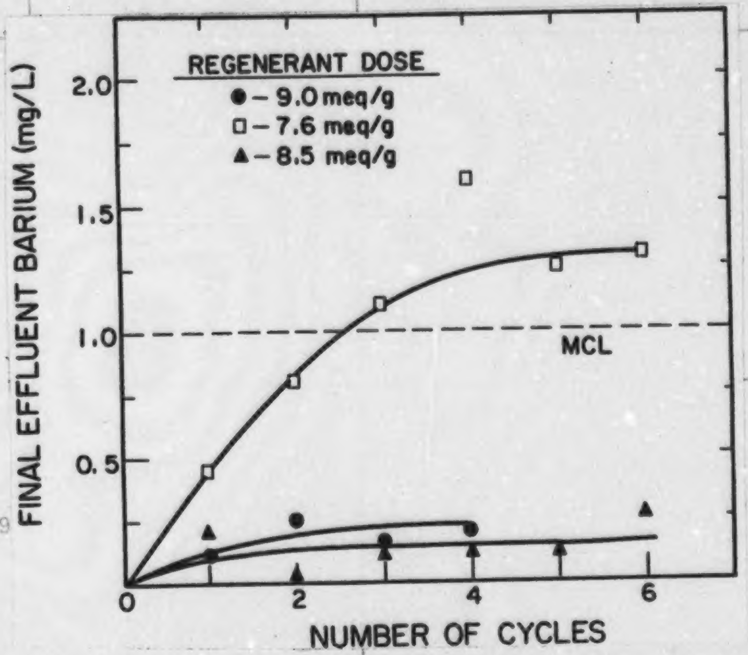

Figure 34. Barium concentration at the termination of weak acid resin cyclic tests.

For regenerant doses of 8.5 and 9.0 meq HCl/g, the barium concentration levels off considerably below the MCL of 1.0 mg/L. On the other hand, when a regenerant dose of 7.6 meq HCl/g was applied as in cyclic test #2, concentrations of barium were found to be greater than 1.0 mg/L. The optimum dose for the water treated in these experiments lies between 7.6 and 8.5 meq/g, and quite likely is about 8 meq/g. This value is also likely to be a function of the quality of water treated and probably will vary with the ratios of barium to hardness, hardness to alkalinity, and hardness to other divalent metal ions. Further research is needed to establish these functions, however.

G. Barium Removal at Crystal Lake, Illinois

Conventional strong acid sodium ion exchange is used at the City of Crystal Lake to remove hardness and barium from its groundwater supply. The

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community obtains its water from wells and treats this water at three sites. The characteristics of one of the two resin columns at site #6 are listed in Table 23.

TABLE 23. DIMENSIONS OF ION EXCHANGE COLUMNS AND REGENERANT DOSES USED AT CRYSTAL LAKE SITE #6

Depth of resin	30"
Free board	23"
Diameter of column	108"
Bed volume	164 ft^3
Type of resin	Permutit Q
Brine concentration	1.32 lb/gal (12% NaCl)
Brine volume	107 ft^3
Brine dose	6.4 lb $NaCl/ft^3$ (4.64 meq/g)
Brine contact time	15 min followed by 15 min rinse

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In July 1982, influent and effluent samples were taken at the two resin columns in use at Crystal Lake's site #6. One influent and three effluent samples were analyzed for sodium, magnesium, calcium, and barium. Concentrations are listed in Table 24. Barium removals ranged from 95.5 to 96.6 percent for an influent of 8.9 mg/L, and were similar to hardness removals which ranged from 89.4 to 94.3 percent for magnesium and 93.9 to 94.9 percent for calcium. Effluent barium concentrations were significantly below the MCL of 1.0 mg/L.

The effluent sodium level ranged from 105-124 mg/L which is expected when strong acid resins are used in the sodium form.

In September 1982, additional effluent samples were analyzed. One of the samples was taken from the column effluent at site #6, another from a hydrant located near the same site, and a third some distance away in the distribution system. The results are shown in Table 25. The ion exchange effluent sample showed a combined hardness of 44.5 mg/L as $CaCO_3$ and a barium concentration of 1.10 mg/L. The July 1982 samples showed not only lower barium concentrations, but also much lower terminal hardness values. The strong acid

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cyclic studies presented above yielded a barium concentration of 1.6 to 1.7 mg/L at a hardness breakthrough of 40 mg/L as $CaCO_3$ for a regenerant dose and influent composition similar to that at Crystal Lake. Thus the barium value of 1.1 mg/L is close to the expected value.

TABLE 24. CRYSTAL LAKE WATER TREATMENT
BARIUM REMOVAL AT SITE #6, JULY 1982

	Na^+ (mg/L)	Mg^{2+} (mg/L as $CaCO_3$)	Ca^{2+} (mg/L as $CaCO_3$)	Ba^{2+} (mg/L)
Influent	13.3	109	123	8.9
Effluent #1	124	6.2	6.3	0.4
Effluent #2	105	11.5	7.5	0.3
Effluent #3	108	9.1	7.3	0.3

Effluent #1 from column 1 after regeneration

Effluent #2 from column 2 after 150,000 gallons processed

Effluent #3 from column 2 after 170,000 gallons processed

TABLE 25. CRYSTAL LAKE WATER TREATMENT BARIUM IN THE DISTRIBUTION SYSTEM AND IN THE COLUMN EFFLUENT AT SITE #6, SEPTEMBER 1982

	Mg^{2+} (mg/L as $CaCO_3$)	Ca^{2+} (mg/L as $CaCO_3$)	Ba^{2+} (mg/L)
Ion exchange column effluent	24.3	20.2	1.10
Hydrant	13.6	11.5	0.80
Distribution system	18.1	20.2	2.00

The hydrant and distribution system samples yielded relatively high barium levels when compared to the column effluent at site #6. The reason for these values was not determined but may have been caused by water from one of the other sites which was not treated as well.

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In November 1982, influent and effluent samples were analyzed for the ion exchange columns in use at sites #7 and #8. Effluent samples were taken just before and just after regeneration, and results of their analysis are given in Table 26. The samples from site #7 showed removal of hardness and barium similar to that at site #6. Barium concentrations were considerably below 1.0 mg/L both before regeneration and after regeneration. The combined hardness prior to regeneration was only 3.0 mg/L as $CaCO_3$.

Samples analyzed from site #8 showed that barium and hardness removal were more of a problem than at the other two sites. The effluent quality after regeneration was acceptable with a combined hardness level of 21.7 mg/L as $CaCO_3$ and a barium level of 0.4 mg/L. However, the water quality prior to regeneration was considerably worse with a hardness of 153.0 mg/L as $CaCO_3$ and a barium concentration of 6.4 mg/L. It is evident that the column is being run well past the normal hardness breakthrough used in softening operations. Consistent with the results from the strong acid cyclic runs, the high hardness and barium concentrations occur together. The regenerant dose of 6 lb $NaCl/ft^3$ was also somewhat lower than the 6.5 lb/ft^3 used at site #6. In February and July of 1983 additional samples at site #8 (see Table 26) led to the same conclusion. It appears that termination of the column run at site #8 before significant hardness breakthrough, and possibly increasing the regenerant dose, would lead to much lower barium concentrations. Based on the results of the cyclic studies, it should be possible to achieve values less than the MCL of 1.0 mg/L.

H. Barium Removal by Home Water Softeners

Various household (Culligan) water softeners in the Crystal Lake and Lake Zurich areas of northern Illinois were sampled at random, without regard to degree of exhaustion, to examine their barium removal efficiencies. The samples were taken by a Culligan representative and sent to the University of Illinois for analysis. Influent and effluent samples were analyzed for hardness and barium and the results are listed in Table 27.

The influent barium concentrations ranged from 0.5 to 6.4 mg/L and influent hardness varied from 205 to 248 mg/L as $CaCO_3$. Effluent samples contained between 0.1 and 0.7 mg/L of barium and 2 to 35 mg/L of hardness

TABLE 26. HARDNESS AND BARIUM REMOVAL AT CRYSTAL LAKE SITES #7 AND #8

	Well #7			Well #8		
	Magnesium (mg/L as $CaCO_3$)	Calcium (mg/L as $CaCO_3$)	Barium (mg/L)	Magnesium (mg/L as $CaCO_3$)	Calcium (mg/L as $CaCO_3$)	Barium (mg/L)
Influent, November 1982	96.3	110.7	11.9	61.7	75.6	11.1
" February 1983				99.6	123.4	20.4
" July 1983				92	153	18.5
Effluent just before regeneration, Nov. 1982	1.0	2.0	0.3	91.4	61.6	6.4
" " " Feb. 1983				36.2	22.4	2.9
" " " July 1983				107.3	91.5	7.4
Effluent just after regeneration, Nov. 1982	4.5	4.5	0.5	14.0	7.7	0.4
" " " July 1983				3.8	8.3	0.2
Effluent after 75,000 gal processed, July 1983				6.0	6.0	0.1

Note: At site #8, 350,000 gallons are usually processed per run.

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as $CaCO_3$. Similar to the results from the municipal system and the cyclic studies, low effluent hardness corresponded well to low effluent barium concentrations.

TABLE 27. BARIUM REMOVAL BY HOME WATER SOFTENERS

a. Crystal Lake, Illinois

Total Hardness (mg/L as $CaCO_3$)			Barium (mg/L)		
Influent	Effluent	% Removed	Influent	Effluent	% Removed
220	35	84	4.8	0.7	85
220	15	93	1.0	0.1	90
210	15	93	6.4	0.1	98
205	10	95	3.0	0.1	97
225	15	93	3.7	0.1	97
225	10	96	4.1	0.1	98

b. Lake Zurich, Illinois

Total Hardness (mg/L as $CaCO_3$)			Barium (mg/L)		
Influent	Effluent	% Removed	Influent	Effluent	% Removed
248	2	99	0.5	0.2	60

I. Radium Removal by Ion Exchange Resins

1. Strong Acid Virgin Resin Column Studies

The ^{226}Ra removal efficiency of the strong acid resin was determined using the virgin resin in the hydrogen form. The Ca^{2+}, Mg^{2+} and Ba^{2+} removals were presented above (see Figure 20) and the ^{226}Ra data given here are for the same run. The influent ^{226}Ra averaged 18.5 pCi/L; Table 28 lists the effluent concentration values along with the total hardness, barium, and sodium concentrations in the effluent samples. The data show that ^{226}Ra removal continued long after saturation of the column with hardness ions.

The radon emanation technique for the measurement of ^{226}Ra was used which has a minimum detectable concentration of 1.0 pCi/L from the 100 mL samples used in this study. The measured values were very close to the detection limit so their precise value is in question. However, all samples were considerably below the MCL of 5 pCi/L.

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TABLE 28. RADIUM REMOVAL, SECOND STRONG ACID VIRGIN RESIN COLUMN TEST

Influent Applied (BV)	Effluent ^{226}Ra (pCi/L)	Effluent Na^+ (mg/L)	Effluent Hardness (mg/L as $CaCO_3$)	Effluent Ba^{2+} (mg/L)
25	1.4	0	0	0
380	2.1	112	0	0
881	2.3	36	214	0
1121	2.0	46	200	0
1622	2.7	47	201	1.0

These samples were analyzed in the Environmental Research Laboratory, University of Illinois, Urbana, IL.

2. Weak Acid Virgin Resin Column Studies

During column test #2 with virgin resin (see Section 5.D for a discussion of its performance), 100 mL samples were collected and analyzed for ^{226}Ra. The influent concentration averaged 18.6 pCi/L while the influent hardness averaged 193 mg/L as $CaCO_3$. Effluent levels for radium and hardness are listed in Table 29. The effluent concentrations are below the MCL of 5 pCi/L. As with the strong acid resin, there is no significant increase in ^{226}Ra concentration long after hardness breakthrough.

TABLE 29. RADIUM REMOVAL, SECOND WEAK ACID VIRGIN RESIN COLUMN TEST

Bed Volumes of Influent	Effluent Hardness (mg/L as $CaCO_3$)	Effluent Radium (pCi/L)
25.6	<1.0	2.5
426.2	<1.0	2.8
671.9	<1.0	3.1
915.5	108	3.0
986.6	148	3.2
1167.1	198	3.0

NOTE: These samples were analyzed in the Environmental Research Laboratory, University of Illinois, Urbana, IL.

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3. Strong Acid Cyclic Column Studies

Influent, effluent, and regeneration samples from several cycles of the sodium form resin column were analyzed for radium^{226}. Using one liter samples and the radon emanation technique, the detection limit for ^{226}Ra is 0.1 pCi/L. For runs 1 through 11, the regenerant dose was 6.5 lb NaCl/ft^3 of resin and for runs 12 through 19 the regenerant dose was 9.75 lb NaCl/ft^3 (see Section 5.E for a discussion of barium and hardness removal). The results are shown in Table 30.

Excellent radium removal by the column was observed for each of the runs. After the 11 cycles at the lower regenerant dose, the column still produced product water with an average radium^{226} concentration of 0.1 pCi/L. After eight additional cycles of the column at the higher regenerant dose, the average radium^{226} concentration in the product water was below 0.1 pCi/L. Throughout each cycle the radium^{226} concentration in the effluent was quite low, and at no point did the concentration exceed the MCL of 5 pCi/L.

Table 31 shows the amount of radium^{226} removed when the column was regenerated. An accumulation of radium^{226} on the resin was observed, but the accumulation per cycle decreased with each successive cycle. After 11 cycles at a regenerant dose of 6.5 lb NaCl/ft^3 of resin, almost 85 percent of the radium^{226} adsorbed during the 11th cycle was removed. After eight additional cycles at a regenerant dose of 9.75 lb NaCl/ft^3 of resin, close to 95 percent of the radium adsorbed during the 19th (and last) cycle was removed by regeneration.

The small accumulation of radium^{226} on the column will not affect resin capacity. During the entire 19 runs of the cyclic test, 29,800 pCi of radium^{226} was passed through the column. Even if all of the radium accumulated, with 1.026 x 10^{-12} g of radium^{226} present for each pCi of alpha radiation, and 2000 meq radium^{226}/226.03 g radium^{226}, only 2.7 x 10^{-7} meq of radium would be on the column - a negligible amount when considering the resin capacity of approximately 5.0 meq/g.

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TABLE 30. RADIUM REMOVAL, STRONG ACID RESIN CYCLIC TESTS

	Influent Applied (BV)	$Radium^{226}$ (pCi/L)	Total Hardness (mg/L as $CaCO_3$)
Cycle No. 1			
Influent		19.1	195
Point Effluent	420	0.3	39
Average Effluent	425	0.1	2.3
Cycle No. 4			
Influent		8.4	209
Point Effluent	8	0.3	1.1
Point Effluent	264	0.2	43
Average Effluent	270		2.6
Cycle No. 6			
Influent		17.7	199
Point Effluent	6	<0.1	1.7
Point Effluent	164	0.3	1.2
Point Effluent	254	0.3	30
Average Effluent	259	<0.1	1.6
Cycle No. 11			
Influent		18.2	216
Point Effluent	27	<0.1	0.8
Point Effluent	182	<0.1	0.8
Point Effluent	248	3.0	23
Average Effluent	255	0.1	1.7
Cycle No. 19			
Influent		18.4	200
Point Effluent	5	0.2	0.4
Point Effluent	216	<0.1	0.4
Point Effluent	261	0.1	4.6
Point Effluent	287	0.7	26
Average Effluent	295	<0.1	1.6

Cycles 6 through 11 were analyzed in the Environmental Research Laboratory, University of Illinois, and cycles 1 through 4 were analyzed in the University Hygienic Laboratory, University of Iowa.

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TABLE 31. RADIUM ACCUMULATION, STRONG ACID RESIN CYCLIC TESTS

Run No.	Waste Brine ^{226}Ra (pCi/L)	Waste Brine Produced (BV/100 BV Product Water)	Percent ^{226}Ra Removed During Regeneration
4	274	2.30	
6	418	2.37	56.0
11	639	2.41	84.8
19	846	2.05	94.4

4. Weak Acid Cyclic Column Studies

The performance of the weak acid resin for radium^{226} removal was also measured during the three cyclic column tests (see Section 5.F for a discussion of the performance of hardness and barium removal). Influent and effluent samples were analyzed for a number of the runs in each of the three tests; the effluent samples were composites of the entire exhaustion cycle. The results are given in Table 32. Removal percentages were comparable for all three cyclic tests, and varied between 90-98 percent. Regenerant dose varied from 7.6 to 9.0 meq HCl/g and seemed to have little effect on removal. Effluent concentrations varied from 0.4-2.0 pCi/L, which are well below the MCL of 5 pCi/L. These results are similar to those for the strong acid resin.

TABLE 32. RADIUM REMOVAL, WEAK ACID RESIN CYCLIC TESTS

Cyclic Test #	Run #	Influent	Effluent	% Removed
1	3	19.3*	2.0*	90
	4	16.1*	0.8*	95
2	4	18.5	0.7	96
	6	16.0		
3	1	19.1	0.4	98
	2	20.0	0.6	97

*130 mL samples were analyzed for these samples, all others were 1000 mL.

NOTE: Samples were analyzed by the Environmental Research Laboratory, University of Illinois, Urbana, IL.

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Since radium^{226} removal occurred even after the resin was saturated with hardness during column test #2 with virgin resin, it appears that the weak acid resin has a very high selectivity for radium. To determine whether the ^{226}Ra was held so tightly that it could not be removed during regeneration, the mass of ^{226}Ra removed during regeneration was determined and compared to the amount that was applied (see Table 33). The mass of radium applied was determined from the influent concentration and the volume of influent applied, while the mass of radium removed was measured by the volume of spent regenerant brine and rinse and its concentration. The amount that passed through the column during the exhaustion cycle was assumed to be negligible. The mass removed is approximately equal to the mass applied so there is no indication of significant accumulation on the weak acid resin.

TABLE 33. RADIUM MASS APPLIED VS. MASS REMOVED DURING REGENERATION OF WEAK ACID RESINS

Cyclic Test	Cycle	Mass Applied (pCi)	Mass Removed During Regeneration (pCi)	% Applied that was Removed
2	4	3735	-	
	6	3125	3830	123
3	5	3456	3479	101
	6	3627	3181	88

NOTE: Samples were analyzed by the Environmental Research Laboratory, University of Illinois and the University Hygienic Laboratory, University of Iowa.

3. Radium Removal by Home Water Softeners

A total of four home water softeners were sampled in Diamond and Biggsville, Illinois, two communities reported as having high levels of radium in their raw water, to determine their efficiencies for radium removal. Samples were taken randomly from the softeners by a Culligan representative and sent to the University of Illinois for analysis. There was no determination as to where in the softening cycle the effluents were sampled or how long the resin had been in use. The hardness and radium concentrations that were measured are listed in Table 34. They show that the water softeners effectively remove ^{226}Ra to concentrations below the standard of 5 pCi/L.

TABLE 34. HOME WATER SOFTENER SAMPLES FOR ^{226}RA REMOVAL

a. Diamond, Illinois	Hardness, mg/L as $CaCO_3$		Radium^{226}, pCi/L	
	Sample 1	Sample 2	Sample 1	Sample 2
Influent	393	417	12.1	
Effluent	7	7	0.4	0.5
Percent Removal	98.2	98.3	96.4	
b. Biggsville, Illinois				
Influent	657	682	9.5	3.3
Effluent	77	122	1.1	2.5
Percent Removal	88.3	82.1	89.4	24.2

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J. Cost Evaluation

Water treatment costs for hardness, radium and barium removal by strong acid sodium form and weak acid hydrogen form ion exchange systems were determined and compared. The major emphasis of the cost analysis was on small water treatment systems, with capacities between 10,000 GPD and 1 MGD. Systems were designed based on the experimental parameters used and determined during column tests.

A flow scheme similar to that shown in Figure 3 for the Cheam Water Plant, was used for the weak acid systems. The strong acid sodium form systems were designed with the same treatment steps except that CO_2 stripping was excluded since no carbon dioxide is created during sodium exchange.

Design of weak acid and strong acid exchange columns was based on the influent characteristics used in column tests and a regeneration frequency of once per day. Usable weak acid resin capacity was determined to be 3.0 eq/L when a regenerant dose of 8.5 meq/g was applied. In experiments reported above (Section 5.E) for a regenerant dose of 4.72 meq/g (6.5 lb $NaCl/ft^3$), the usable strong acid resin capacity was 0.9 eq/L (2.77 meq/g).

Using the design requirements determined in our laboratory experiments, Illinois Water Treatment (IWT) Company (Rockford, IL) personnel determined process costs for strong acid sodium form and weak acid hydrogen form exchange

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units. The strong acid ion exchange units included the columns, the resin, regenerant day tanks, brine tanks and interface piping. The weak acid unit included all of these plus a carbon dioxide stripping tower. A comparison of the two types of exchange systems was used to evaluate the additional costs required for weak acid exchange systems with capacities of 0.01, 0.1, and 1 MGD.

Complete treatment costs, including costs of construction and maintenance materials, power and labor requirements, were determined for sodium exchange softeners using the October, 1978 cost curves by Hansen et al. (1979). The assumed treatment included sodium exchange softening, sodium hydroxide for pH adjustment, chlorine addition and clearwell storage. Cost of strong acid sodium exchange units were determined for columns similar in size to those designed by IWT. Cost of chemical addition was based on treatment plant flow and the sodium hydroxide addition required to adjust the effluent pH to 8.3 and the chlorine in 1.5 mg/L. Clearwell storage requirements were assumed to be 10 percent of the daily flow capacity. Table 35 and Table 38 provide the design criteria and cost calculations for a 100,000 GPD and a 1 MGD system.

Costs were analyzed and updated to March 1983. Capital costs were adjusted using the Engineering-News Record (ENR) Construction Cost Index, while maintenance material costs were updated with the Producer Price Index for Finished Goods. Labor costs, including fringe benefits were determined by Gumerman et al. (1978) to be $10/hr, and were adjusted to March 1983 using the ENR Skilled Labor Index. Chemicals and power were based on costs current in March of 1983. Annual, as well as unit, costs for sodium exchange softening are listed in Table 36 and Table 37 for 100,000 GPD and 1 MGD plants.

Costs do not include costs of raw water, in plant or finished water pumping. Brine disposal was also not included, since costs are dependent on the acceptable means of disposal. When brine can be discharged into a sanitary sewer, disposal is relatively inexpensive. However, means of brine disposal can be considerably expensive and may prevent ion exchange from being economically feasible.

Table 39 shows the complete unit costs of sodium form exchange and the additional unit costs for weak acid hydrogen form exchange. The incremental

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costs for weak acid systems include the differences in process equipment, chemical requirements, and power requirements. Weak acid costs include costs for sulfuric acid regeneration as well as hydrochloric acid regeneration.

TABLE 35. COST CALCULATION FOR 100,000 GPD SODIUM EXCHANGE SOFTENING PLANT, 1978

System and Design Criteria	Construction Cost ($)	Energy Required (kw-hr/yr)	Maintenance Material ($/yr)	Labor (hr/yr)
Pressure Ion Exchange Softening (0.1 MGD)	80,000	14,190	800	1,100
Sodium Hydroxide Feed System (40 mg/L)	12,500	4,900	165	124
Chlorine Feed System (1.5 mg/L)	4,310	4,910	40	183
Clearwell Storage (100,000 gallons)	21,500	0	0	0
Subtotal	118,310	23,280	1,005	1,407
Lightwork, Interface Piping, Roads @ 5%	5,916			
Total Construction Cost	124,226			
General Contractors Overhead and Profit @12%	14,907			
Subtotal	139,133			
Engineering @ 10%	13,913			
Subtotal	153,046			
Legal, Fiscal, and Administrative	5,000			
Interest During Construction (7%)	2,400			
Total Capital Costs	160,446			

TABLE 36. COST CALCULATION FOR 100,000 GPD SODIUM EXCHANGE SOFTENING PLANT, 1983

Item	Total Costs/Year
Amortized Capital @ 7%, 20 years	$20,826
Labor: 1,407 hr @ $14.6/hr	20,545
Electricity: 23,280 kw-hr, @ 0.0674 $/kw-hr	1,569
Maintenance Material	1,426
Chemicals, sodium chloride, 76 tons/year @ $24.50/ton	
Sodium hydroxide, 6.1 tons @ $573/ton	
Chlorine, 0.23 tons @ $370/ton	5,441
Total Annual Cost	$49,807

Unit Cost = 136.5¢/1,000 gallons treated

TABLE 37. COST CALCULATION FOR 1 MGD SODIUM EXCHANGE SOFTENING PLANT, 1983

Item	Total Costs/Year
Amortized Capital @ 7%, 20 years	$ 40,884
Labor: 2,307 hr @ $14.6/hr	33,688
Electricity: 64,090 kw-hr, @ 0.0674 $/kw-hr	4,319
Maintenance Material	7,252
Chemicals, Sodium chloride, 760 tons @ $24.5/ton	
Sodium hydroxide, 61 tons @ $573/ton	
Chlorine, 2.3 tons @ $370/ton	54,424
Total Annual Cost	$140,567

Unit Cost = 38.5¢/1,000 gallons treated

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TABLE 38. COST CALCULATION FOR 1 MGD SODIUM EXCHANGE SOFTENING PLANT, 1978

System and Design Criteria	Construction Cost ($)	Energy Required (kw-hr/yr)	Maintenance Material ($/yr)	Labor (hr/yr)
Pressure Ion Exchange Softening (0.1 MGD)	160,000	69,000	4,900	2,000
Sodium Hydroxide Feed System (40 mg/L)	17,500	9,800	170	124
Chlorine Feed System (1.5 mg/L)	4,310	4,190	40	183
Clearwell Storage (100,000 gallons)	50,000	0	0	0
Subtotal	231,810	64,090	5,110	2,307
Lightwork, Interface Piping, Roads @ 5%	11,591			
Total Construction Cost	243,401			
General Contractors Overhead and Profit @ 12%	29,208			
Subtotal	272,609			
Engineering @ 10%	27,261			
Subtotal	299,870			
Legal, Fiscal, and Administrative	8,000			
Interest During Construction 7%	7,100			
Total Capital Costs	314,970			

Unit costs tend to decrease as the treatment plant size increases due to economics of scale. Since a certain amount of capital is required regardless of treatment size, the capital costs are a large part of the smaller systems. As the size of treatment increases, operational costs and especially chemical costs become a much larger percentage of the overall costs.

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TABLE 39. COST COMPARISON FOR WEAK ACID AND STRONG ACID TREATMENT PLANTS

Treatment Capacity (GPD)	Strong Acid Resin NaCl Regenerant (¢/1000 gal)	Weak Acid Resin HCl Regenerant[a] (¢/1000 gal)	Weak Acid Resin H_2SO_4 Regenerant[a,b] (¢/1000 gal)
10,000	-	+96.7	+83.7
100,000	136.5	+14.7	+ 1.3
1,000,000	38.5	+ 7.9	- 5.1

[a] These costs are in addition to those for use of strong acid resin, NaCl regenerant.

[b] Note: H_2SO_4 has not been used as a regenerant and may not be usable if $BaSO_4$ precipitates in the resin.

Capital costs are much more prominent in weak acid systems due to the increased process equipment. Weak acid systems require more expensive instrumentation for acid regeneration as well as durable materials to withstand low pH. Weak acid systems also require decarbonation which is a significant capital addition. Therefore, weak acid ion exchange is considerably more expensive for smaller operations, but becomes more reasonable as the treatment plant size increases.

It is also interesting to note the difference in weak acid costs when applying sulfuric acid as a regenerant as opposed to hydrochloric acid. Sulfuric acid was not used in any of the column experiments in this study due to the possibility of $CaSO_4$ and $BaSO_4$ precipitation in the resin column. Based on this cost analysis the applicability of sulfuric acid should be examined as a means of regeneration.

Table 39 shows that weak acid ion exchange is actually cheaper than strong acid ion exchange when sulfuric acid is used to regenerate. This is due to the dose of sodium hydroxide required to obtain an effluent pH of 8.3. More sodium hydroxide is required for the product of strong acid sodium exchange to raise the pH due to its high alkalinity. The alkalinity is not changed by sodium ion exchange whereas the alkalinity is reduced to a low level during weak acid hydrogen exchange. If an effluent pH of 7 were acceptable, the chemical costs of strong acid exchange could be significantly reduced.

Water with a low calcium concentration is quite likely to be corrosive, even though soft water with a pH of 7, and high alkalinity water is likely to

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be less corrosive than low alkalinity water. A product that will minimize corrosion is one which results if only a portion of the water is treated by ion exchange and the remainder is by-passed and then blended with the ion exchange effluent. When Ba^{2+} and/or ^{226}Ra is present, it may be necessary to treat all of the water to meet the MCL. In this case, some means should be found to increase the calcium content of the water prior to its distribution through certain types of pipes. Further research is needed to establish the best means of doing this, such as using a parallel column in the calcium form.

K. Activated Carbon Tests

A series of batch tests were performed using three granular activated carbons, Nuchar WV-G, Darco 3000, and Carborundum GAC 1240 to determine which carbon gave the best barium removal. The carbon with the best removal was then used in additional testing to determine if its capacity could be improved. Using 0.5 g of carbon in contact with 100 mL of a 1.0 mM Ca^{2+}, 1.0 mM Mg^{2+}, and 0.22 mM Ba^{2+} solution, and removing part of the sample for analysis after 2, 5, 13, and 20 days, the final concentrations of barium in solution were determined (Table 40).

TABLE 40. BARIUM REMOVAL BY ACTIVATED CARBON

	Barium Concentration After:			
	2 Days	5 Days	13 Days	20 Days
Darco 3000	<0.01 mM	<0.01 mM	<0.01 mM	<0.01 mM
Nuchar WV-G	0.204 mM	0.183 mM	0.178 mM	0.162 mM
Carborundum 1240	0.199 mM	0.155 mM	0.131 mM	0.131 mM

Darco 3000 showed the greatest removal of barium and was therefore used in additional testing. Treating 5 g of carbon with 500 mL of 3.6 N, 1.8 N, or 0.36 N H_2SO_4 solutions and then contacting 0 to 0.5 g of carbon with 100 mL of 100 mg/L Ba^{2+} (0.73 mM) solution gave the isotherms shown in Figure 35. Though the results are preliminary and there is very little difference between the curves for 1.8 N and 0.36 N acid treatment, the use of an acid treatment does elevate the barium removal. Carbon treated with a 3.6 N acid solution removed up to 26 mg Ba^{2+} per gram of carbon while the untreated carbon only removed 14 mg/g.

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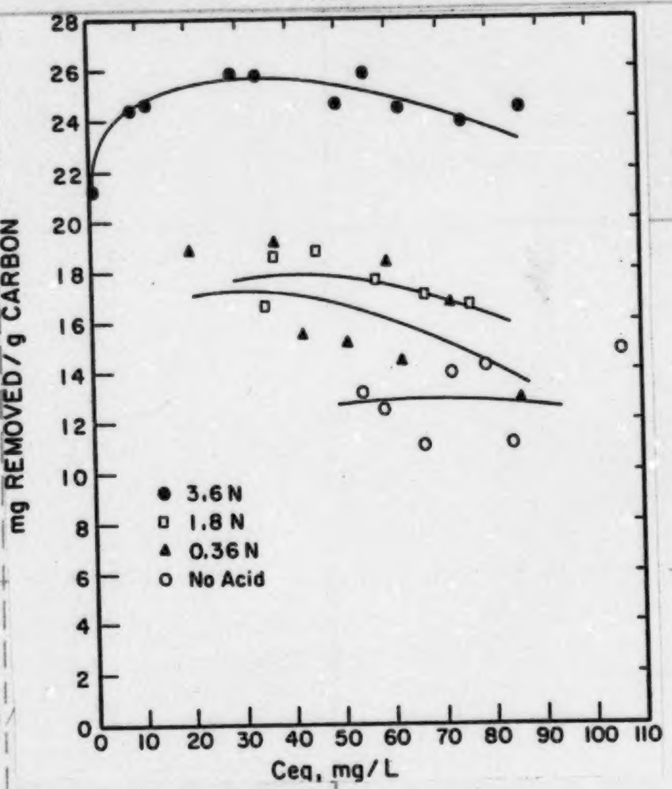

Figure 35. High concentration barium isotherms on activated carbon.

Similar tests were performed with the same carbon and a solution containing 1.0 mM Ca^{2+}, 1.0 mM Mg^{2+}, and 20 mg/L (0.15 mM) Ba^{2+}. Figure 36 shows the amount of barium removed from solution after treatment of the carbon with various acid solutions. These preliminary results cannot be used to easily distinguish between the various acid solutions, but carbon treated with acid will remove as much as 14 mg/g whereas the untreated carbon removes less than 10 mg/g. No detectable amounts of magnesium and calcium were removed.

Assuming a column of activated carbon treated with H_2SO_4 could have a capacity of 14 mg/g, and that carbon costs 70¢/lb, the cost of the carbon required to treat 1,000 gallons with 20 mg/L of barium would be $8.30. Untreated carbon would result in a cost of $11.67 per 1,000 gallons. Because of this high cost further testing does not appear warranted.

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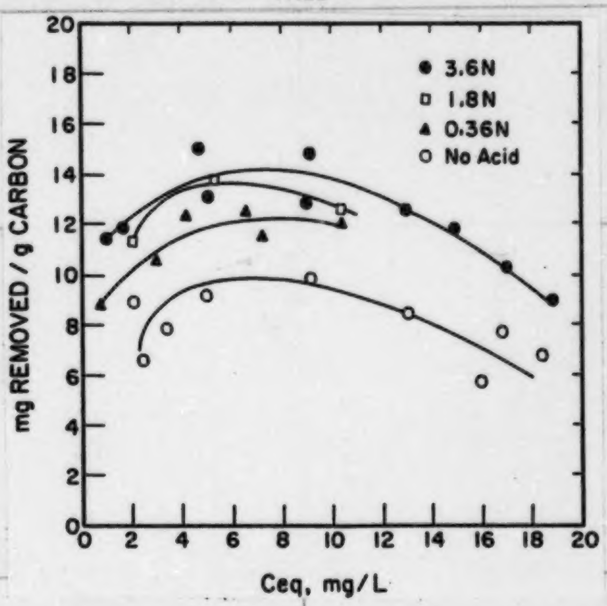

Figure 36. Low concentration barium isotherms on activated carbon.

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